C-O-N-F-I-D-E-N-T-I-A-L | SEE BOTTOM OF PAGE FOR SPECIAL CONTROLS, IF ANY

INFORMATION REPORT

PREPARED AND DISSEMINATED BY
CENTRAL INTELLIGENCE AGENCY

COUNTRY
USSR

SUBJECT
Radiochemical Research in the USSR/The Use of Tracer Atoms in the Physico-Chemical Study of Some Inorganic Polycompounds

50X1-HUM

50X1-HUM

DATE DISTRIBUTED 2 April 58

NO. OF PAGES 1 NO. OF ENCLS. 50X1-HUM

SUPPLEMENT TO REPORT #

50X1-HUM

THIS IS UNEVALUATED INFORMATION

50X1-HUM

[redacted] copies of two scientific papers [redacted] by Victor Spitsyn, USSR scientist [redacted] 50X1-HUM Prof Spitsyn is a member of the faculty of Moscow University and a Corresponding Member of the USSR Academy of Sciences. The titles of the two papers are:

50X1-HUM

"Radiochemical Research in the USSR".

"The Use of Tracer Atoms in the Physico-Chemical Study of Some Inorganic Polycompounds"

[redacted]

50X1-HUM

- end -

C-O-N-F-I-D-E-N-T-I-A-L

DISTRIBUTION	STATE	ARMY	NAVY	AIR

NOFORN NO DISSEM ABROAD LIMITED

LIMITED: Dissemination limited to full-time employees of CIA, AEC and FBI; and, within State and Defense, to the intelligence components, other offices producing NIS elements, and higher echlons with their immediate supporting staffs. Not to be disseminated to consultants, external projects or reserve personnel on short term active duty (excepting individuals who are normally full-time employees of CIA, AEC, FBI, State or Defense) unless the written permission of the originating office has been obtained through the Assistant Director for Central Reference, CIA.

04-03-61

RADIOCHEMICAL RESEARCH IN THE USSR

By Victor Spitsyn,

Professor of Moscow University, Corresponding Member of the USSR Academy of Sciences.

Studies of radioactive elements began in Russia soon after radioactivity had been discovered. They were conducted in close cooperation between scientists of various specialities: mineralogists, physicists, chemists, technologists and physicians.

The physicists A.P.Sokolov (1903) and I.I. Borgman (1904) studied the radioactivity of various natural objects - mineral water, medicinal mud, rock and soil, and considerably improved the methods of radiometry. A.P.Sokolov notably developed a compensation method for determining radium by radon, which subsequently found wide application.

N.A.Orlov (1904) discovered radiation-chemical transformations of paraffin and other organic substances during the action of radium emanation. Y.N.Antonov (1913) discovered a new radioelement, uranium X, among the products of decay of uranium. L.S.Kolovrat-Chervinsky (1914) conducted major research on the isolation of radium emanation by solid and molten salts. Vl. I. Spitsyn (1917) used radioactive tracer atoms (RdTh, UX1) to measure the solubility of slightly soluble compounds of thorium.

I.A.Antipov (1900) discovered a uranium deposit in the Ferghana Region, the first in Russia. V.I.Vernadsky (1910) organized a series of expeditions aimed at a wide-scale research of

uranium-radium and thorium ores and undertook an extensive study of the geochemistry of radioelements. Kh.I. Antipovich (1908) carried out experimental refining of Russian uranium-vanadium ores, but the attempts to isolate radium from it encountered great difficulties.

Even at that time Russian scientists took full account of the importance of research in the field of radioactive elements. In 1910, V.I.Vernadsky (1) wrote: "Today sources of atomic power are revealed before us in the phenomena of radioactivity, exceeding millions of times those which man's imagination could picture, sources which by their power and importance dwarf the power of steam, electricity and chemical explosion processes .... Mankind has entered the new age of radiant, i.e. atomic, power." The level of industrial production was, however, very low in prerevolutionary Russia. As a result, the material and engineering opportunities for the advancement of research, notably, on radiochemistry, were greatly limited.

The situation has abruptly changed after the Great October Socialist Revolution. One of the first tasks set by the Soviet government in 1918 before the Academy of Sciences was to elaborate a method for extracting radium out of Soviet uranium-vanadium ores. The task, difficult at the time, was successfully resolved under the guidance of V.G.Khlopin, an outstanding Russian chemist, and in 1921 the staff of the Experimental Radium Plant produced the first ~~preparation~~ sample of radium bromide.

The production of pure compounds of uranium was started in the USSR a few years later on the basis of these raw materials.

The further development of radiochemistry in the USSR was closely connected with the activities of the Radium Institute founded in 1922 and attached to the Academy of Sciences. Under the guidance of V.G.Khlopin, the mechanism of the process occurring in fractional crystallization of barium-radium salts was investigated, the knowledge of which proved indispensable in ensuring the progress of the Soviet radium industry.

According to the rule evolved long ago by K.Fajans-F.Paneth (1913), a radioelement in solution in a state of microconcentration is supposed to be absorbed by the precipitate if the element forms with an ion of the reverse sign of the solid phase a compound which is difficult to dissolve in the given medium. In 1924, Khlopin (2) proved that isomorphism of the solid phase and the radium salt so formed is an indispensable condition of such coprecipitation, while the degree of solubility is of no considerable importance. For example, during the crystallization of gypsum out of a solution, the radium present there does not pass into the solid phase as gypsum and radium sulphate are not isomorphous. Anhydrous strontium nitrate isolated from aqueous solutions at a temperature above 34° is isomorphous with radium nitrate and captures it in the course of crystallization. On the other hand, with a temperature below 34°C, when the hydrate $Sr(NO_3)_2 \cdot 4H_2O$, is formed, which is

not isomorphous with radium nitrate, the latter is not included at all in the solid phase. If, however, crystallization of strontium nitrate is carried out at 0°C, the isolated crystals of $Sr(No_3)_2 \cdot 4H_2O$ again begin to capture radium as a result of forming tetrahydrate of radium nitrate, similar to barium, which does not exist in a free state but which is capable of producing isomorphous mixtures with $Sr(No_3)_2 \cdot 4H_2O$.

V.G.Khlopin was the first to employ quantitative physicochemical methods to study two-phase systems, of the type salt-water, containing a microcomponent. It was demonstrated that during crystallization equilibrium is attained much slower by the microcomponent than by the macrocomponent. This pointed to the great role played by the process of residue recrystallization, which occurs for a long period of time, after the apparent equilibrium between the macrocomponent and the solution has already set in, and which replaces the phenomenon of diffusion, practically absent in the solid phase.

V.G.Khlopin (3) and his associates made a study of over 30 systems containing compounds of strontium, barium, lead, cerium, uranium, etc. as a macrocomponent, and radium, polonium, and lead, bismuth and thorium isotopes (RaD, RaE and UX_1) as a microcomponent. It appeared in every case under investigation that the microcomponent producing a compound isomorphous with the solid phase is distributed between the crystals and the solution like a diluted substnace between two non-mixing sol-

vents (V.G.Khlopin, 1924).

The following formula was suggested for quantitatively ~~appraising~~ estimating the distribution of radium between the crystals of barium salt and the solution:

$$\frac{x}{m} = K\frac{1-x}{v} \qquad (1)$$

where x is the amount of radium which passed into the crystals, m is the weight of the solid phase, 1 - x is the amount of radium remaining in the solution, v is the volume of the solution, and K is some constant typical of every pair of salts.

Subsequently V.G.Khlopin and B.A.Nikitin (4) modified the equation in the following way:

$$\frac{xS_1}{m} = K_2\frac{(1-x)S_o}{q} \qquad (2)$$

where x, 1-x and m have the former values, q is the weight of the liquid phase, and S_1 and S_o are the specific weights of the solid and liquid phase.

If one designates by x and 1-x respectively the amount of the microcomponent which passed into the crystals or remained in the solution, and by y and 1-y the amount of the macrocomponent which passed into the crystals or remained in the solution, the process of fractional crystallization may be defined by the following equation:

$$\frac{x}{y} : \frac{1-x}{1-y} = D \qquad (3)$$

where D is the coefficient of fractioning, representing the

ment in the crystals and the coefficient of microcomponent impoverishment in the solution.

In case fractional crystallization proceeds in a normal way, the coefficient of crystallization remains constant and, at the same time, corresponds to equation (3) throughout the process. This regularity was repeatedly checked in practice and served as a scientific basis in controlling and adjusting the industrial methods for isolating radium and some other radioelements.

Proceeding from the ~~doctrine~~ theory of the thermodynamic potential and the theory of activities, A.P. Ratner (5) deduced a theoretically general equation demonstrating the regularity of distribution of the microcomponent between the solid crystal and liquid phases and established a connection between the coefficient of fractioning and the concentrations of the components in the two phases, and the properties of pure components. The equation he obtained proved to fully accord with the experimental data.

The research outlined above has made it also possible to draw the following important theoretical conclusion: the applicability of the law of distribution to the behaviour of some microcomponent between the crystals of some salt and the solution is proof of the presence of isomorphism between the available compound of the microcomponent and the salt forming a solid phase, and of the similarity of their composition and

molecular structure.

This method was, notably, helpful in establishing the existence of non-stable compounds or of those present in small quantities, and in studying their composition and structure. V.G.Khlopin and A.G.Samartseva (6) have proved that polonium in a system containing crystals and a saturated solution of sodium telluride, Na_2Te, is subordinated to the law a distribution and thus isomorphously replaces bivalent tellurium. By transferring $Na_2Te(Po)$ to dibenzyl- telluride, $Te(CH_2C_6H_5)_2$, the investigators proved that in this case, too, polonium followed tellurium. By means of dimethyl sulphate, $Na_2Te(Po)$ was transferred to a volatile compound, namely dimethyltellurium, $Te(Po)(CH_3)_2$. This helped in finally proving the existence of bivalent polonium compounds.

By joint crystallization of polonium with the salts of telluric acid, $PbTeO_4$ and $K_2TeO_4 \cdot 3H_2O$, in a similar way, A.G.Samartseva (7) was the first to prove the existence of hexavalent polonium forming the anion PoO_4^{2-} in oxidizing media.

By using the method of isomorphous coprecipitation, B.A.Nikitin (8) obtained valuable data on the chemical compounds of radon and other inert gases. The hydrate of sulphur dioxide of the composition $SO_2 \cdot 6H_2O$, when below its eutectic point (-2.6°), proved to absorb radon even in its negligible concentration (10^{-12} g/cm^3). Pure ice does not exhibit such a

phenomenon. The ratio of radon and sulphurous anhydride in the gaseous and crystalline phases ~~is subordinated to~~ follows the law of distribution. It has thus been established that radon forms a hydrate isomorphous with the hydrate of So_2 and ~~according~~ corresponding by its composition ~~with~~ to the formula $Rn.6H_2O$. Radon is absorbed in a similar way by the solid hydrate of hydrogen sulphide $H_2S.6H_2O$. Nikitin calculated that the ~~resilience of~~ pressure of dissociation of radon hydrate amounts to 760 mm at about 0^oC. Hence, pure radon should interact in such conditions directly with ice, forming a hydrate.

Similar phenomena were discovered by Nikitin for other inert gases, namely, argon and neon. The coefficient of distribution depends on the nature of inert gases. The greater their atomic radii and the higher ~~the capacity for~~ polarization, the stronger the hydrates so formed. In the case of the inert gases investigated by Nikitin, the coefficients of distribution between the gaseous phase and the solid hydrate, $So_2.6H_2O$, had the following values:

	Rn	Ar	Ne
D =	0.57	0.0078	0.00004

When the solid phase attains uniformity, during the transition of 99% of the sulphur dioxide under examination to the residue, absorption is recorded of 98.3% of the radon, 43.6% of the argon, 0.4% of the neon and less than 0.01% of the helium present in the gas mixture. By precipitating the

hydrate of SO_2 in several stages and controlling the temperature, it is possible to separate inert gases in this chemical way.

Subsequently B.A.Nikitin (9,10) succeeded in proving in the same way the formation of radon compounds with toluene, and of phenol with parachlorophenol, such as $Rn.2C_6H_5CH_3$, $Rn.2C_6H_5OH$, $Rn.3ClC_6H_4OH$. The compounds $HBr.2C_6H_5CH_3$, $H_2S.2C_6H_5OH$ and $H_2S.3ClC_6H_4OH$ were used as carriers. Radon is not, however, captured by molecular compounds of the type of $AlBr_3.H_2S$, apparently as a result of a strongly pronounced polarity of such substances.

A ~~profound~~ Lazi study of the phenomena of coprecipitation of various substances according to Khlopin's method has made it possible to obtain new valuable information on the nature of isomorphism and to apply them to the processes of separation of radio elements. V.G.Khlopin and B.A.Nikitin (11) investigated in this way the phenomena of isomorphism of the second kind, when isomorphous replacement takes place in the case of a similar chemical type of the substance structure, though irrespective of their chemical analogy. This includes isomorphism in such systems as $BaSO_4$ - $KMnO_4$, $BaCrO_4$ - KBF_4, NaBr - PbS, etc. Using as examples the systems containing potassium perchlorate and sulphate of the radioactive isotope of lead (RaD), rubidium perchlorate and radium sulphate ($RbClO_4$, $RaSO_4$), Khlopin and Nikitin proved that at a concentration of the order

of 10^{-6} %, lead and radium do not enter the crystal lattice of perchlorates. It has been thus established that in the case of isomorphous replacements of the second kind there exists a lower ~~boundary~~ limit of mixing. At the same time the perchlorates under investigation were capable of capturing radium or lead sulphates if the latter had a concentration sufficient for the building of their own crystal lattice. This leads to a conclusion of great scientific significance: in the case of real isomorphism, the replacement proceeds ion for ion, atom for atom or molecule for molecule; but in the case of isomorphism of the second kind, the replacement is carried out by whole sections of the crystal lattice, to an amount ranging from one elementary cell to a comparatively large number of cells.

V.G.Khlopin (12), B.A.Nikitin (13) and their associates also studied by the above method the various systems forming the so-called anomalous mixed crystals whose components differ not only by their chemical formula, but frequently by their crystal shape as well, such as NH_4Cl-$FeCl_3$, $BaI(NO_3)_2$ - Methylene Blue, K_2SO_4 - Crystal-Ponsol dyestuff, etc. It appeared that in this case, too, the lower ~~boundary~~ limit of mixing was recorded. Hence, anomalous mixed crystals possess a micro-dispersed mosaic structure, but in the course of their isolation there remains a constant value of the crystallization coefficient.

V.G.Khlopin and M.S.Merkulova (14) discovered a lower

boundary of mixing also during coprecipitation of radium and thorium (in the case of UX_1) with lanthanum fluoride. Hence, anomalous mixed crystals are formed in the systems LaF_3 - RaF_2 and LaF_3 - ThF_4.

Interesting data were obtained by M.S.Merkulova (15) in studying a more complex case, namely the coprecipitation of bivalent metal ions with salts of the type of NaCl. No lower boundary of mixing was found in this case. In the systems NH_4I - PbI_2 - H_2O, NaCl - $PbCl_2$ - H_2O and NaCl - $SrCl_2$ - H_2O, the diatribution of the microamounts of lead and strontium isotopes (Sr^{89}) occurs in such a way that the crystallization coefficient, D, is a constant, irrespective of the amount of the solid phase ~~isolated into the residue~~ precipitate, and of the presence of foreign ~~high~~ multi-valent ions in the solution. Analysis of the speed at which equilibrium was established by the microcomponent in the system NaCl - $PbCl_2$ - H_2O demonstrated that equilibrium was attained during a long ~~time~~ period of (for over 30 hours). This is in accordance with the mechanism of formation of solid solutions. In the case under examination, the microcomponent enters the crystal lattice of the macrocomponent salt only up to a certain limit (the upper boundary of mixing). The results

mixing. This is a new type of coprecipitation, which cannot be classified as any of the types already known.

In the course of the given analysis it was established the crystallization coefficient for lead possesses a very high value (D_{Pb} = 220 at 25°C). It was possible to use this phenomenon to separate small amounts of isotopes of lead (ThB, RaD) and bismuth (RaE). The latter are distributed between the crystals and the saturated solution of sodium chloride, independent of one another and with their own coefficients of distribution, which ~~quite~~ strongly differ by their absolute value (D_{Bi} = 0.4). When 5% of NaCl is isolated from an oversaturated solution, 96.8% of RaD and 2.9% of RaE pass into the ~~residue~~ precipitate. After repeated precipitation, 93.7% of RaD and 0.06% of RaE are concentrated in the residue. Complete separation of the isotopes of lead and bismuth may be attained by applying the method of isothermal evaporation of the saturated solution of sodium chloride, containing microquantities of $PbCl_2$ and $BiCl_3$.

M.S.Merkulova (16) and her associates have also analysed recently the processes of coprecipitation, attended with the formation of inner adsorption systems. A study has been made of the systems $K_2SO_4 - PbSO_4 - H_2O$, $K_2SO_4 - RaSO_4 - H_2O$ and $K_2CrO_4 - PbCrO_4 - H_2O$. It appeared that there occurred a regular capture of the microcomponent by the solid phase

when crystals of sodium sulphate and potassium chromate are isolated out of the solution in the presence of lead and radium. In this case the behaviour of lead and radium isotopes is likewise subordinated to the law of distribution, and the crystallization coefficient, D, has a constant value. The speed of establishing equilibrium, amounting to but 5-10 minutes, points, however, to the absorption nature of the phenomenon. The presence of easily adsorbed high-valent ions in the solution greatly reduces the coefficient of crystallization. This phenomenon draws a sharp distinction between coprecipitation attended with the formation of inner adsorption systems the one in the shape of isomorphous and anomalous mixed crystals. For example, an increase in the concentration of Bi^{3+} ions up to 0.1 mg/ml and of Al^{3+} ions up to 0.02 mg/ml completely stops the transition of lead and radium isotopes to potassium sulphate and chromate crystals.

The research carried out by V.G.Khlopin and his pupils and associates have considerably enhanced our knowledge regarding the behaviour of radioelements in an ultra-diluted state, when various crystal residues are precipitated from the solutions.

It should be noted that the distribution of microamounts of radioelements between molten salts and the solid crystalline phase is, in the main, subordinated to the regularities dis-

covered in the case of solutions. D, the coefficient of crystallization, remains a constant value, irrespective of the amount of the precipitated solid phase and the method of its precipitation. V.G.Khlopin and B.R.Klokman (17, 18) have proved this when studying a number of systems containing barium, lead, strontium and calcium salts as a macrocomponent, and radium, ThX and ThB as a microcomponent. Molten systems also exhibited the formation of anomalous mixed crystals (LaF_3 - RaF_2) and inner adsorption compounds (K_2SO_4 - $RaSO_4$). At high temperatures the process of recrystallization occurs, however, much faster than in solutions.

There are also some peculiarities in the behaviour of the microcomponents in molten media. $BaCl_2$ proved to produce a continuous series of mixed crystals both with $PbCl_2$ and $SrCl_2$, while $RaCl_2$ coprecipitates only with $PbCl_2$. Hence, there is a sharp difference in the behaviour of radium and barium in this case (19).

A number of investigations were also conducted in the USSR, devoted to the problems of adsorption of radioelements and the formation of radiocolloids. It has long been known that some radioelements exhibit the properties of colloids and can, for example, be separated by means of dialysis. The opinion was, however, ~~voiced~~ expressed that, while in infinitely diluted solutions, radioelements do not form colloidal particles of their own, but are adsorbed on colloidal particles of other

substances, namely compounds of ordinary elements.

I.E.Starik (20) has shown that in polonium compounds the colloidal properties are most pronounced precisely in those media where a minimum of adsorption is observed on preliminarily prepared colloidal particles. This was convincing proof of the fact that polonium forms genuine colloidal solutions. The conditions of their existence have been specified by subsequent research, use being made of centrifuging, ultrafiltration and other research methods (21). It appeared that at concentrations of 10^{-9} - 10^{12} mol/l with pH ranging from 8 to 10, polonium, which is apparently in a quadrivalent state, mostly forms insoluble compounds and under such conditions is detained by ultrafilters to the utmost.

A.P.Ratner (22) and his associates applied the method of centrifuging and dialysis to 10^{-5} M solutions of zirconium, niobium and tantalum compounds tagged with corresponding radioactive isotopes. The hydroxides of the elements under investigation proved to exist in a colloidal state in the range of pH from 1-2 to 12-13. During centrifuging, the colloidal particles of zirconium are separated almost to the full, while niobium and tantalum are practically not isolated. Analysis of centrifuging and ultrafiltration of polonium solutions and of some isotopes of thorium (UX_1 and RdTh) at various values of pH permitted to discover the presence in these solutions

of two groups of particles some scores of microns and about 1/m in size. The radioelement in the ~~shape~~ form of roughly dispersed particles passes through the dialyser, though rather slowly, while the one in the ~~shape~~ form of finely dispersed particles does not pass at all. An assumption has been made that the roughly dispersed particles represent a radioelement adsorbed on impurities, while the finely dispersed particles are formed by the radioelement itself. Partial ionization of the colloid-diluted solid phase of the radioelement appears to play some part in the latter case. After equilibrium has been established between the ionic part of the inner solution and the outer solution, the process of dialysis comes to a stop.

Recently I.E. Starik (23) and his associates have been systematically studying the conditionof small amounts of various radioelements in solutions. The formation of colloids has been established by the method of ultra-filtration with the aid of radioactive isotope Ru^{103} in the case of tri-and quadrivalent ruthenium within a narrow range of pH (5-7), a recharging of colloidal particles being recorded. The absence of a positively charged colloid was proved in the case of trivalent thallium hydroxide when Tl^{2-4} was used as a tracer. With pH amounting to 3, coagulation is recorded, and with pH exceeding 7, a stable negatively charged colloid is formed.

At a concentration of 10^{-11} mol/l, fission zirconium-95 is to be found in acid nitrate solutions as positive ions.

With pH ranging from 1.6 to 4.2, Zr^{95} is markedly adsorbed on negatively charged particles of impurities and behaves like a roughly dispersed colloid. With pH amounting to 4.2, solubility product $Zr(OH)_4$ is attained, and a proper negatively charged zirconium hydroxide colloid is formed, with the particles approximately 1m in size (24).

In the case of uranylchloride in a hydrochloride medium, at a concentration of $5 \cdot 10^{-4}$ mol/l, a colloidal formation of hydrolysis products was found, with pH ranging from 2.5 to 6.5. In the case of concentrations of the order of 10^{-8} mol/l, uranium forms a pseudocolloid, with pH ranging from 2.5 to 6.5, due to the adsorption of the microimpurities on the particles existing in the solution (25).

The above research has greatly clarified the conditions under which real colloids of radioelements and their pseudocolloid solutions are formed.

Investigation into the phenomena of sorption of radioelements likewise attracted much the attention of Soviet researchers. V.G.Khlopin (3) suggested general methods which permit to distinguish isomorphous cocrystallization from adsorption capture; it is necessary to test the speed of establishing equilibrium between the solution and the residue by the radioelement, once, by precipitating the solid phase from the solution containing the radioelement, and the second time, by adding a preliminarily precipitated residue to the

solution. In the case of isomorphous coorystallization, the magnitudes so found sharply differ from one another, while during adsorption capture they approximate one another. Apart from this, the process of recrystallization influences in a different way the relative amount of the radioelement which has passed into the solid phase: if isomorphous coorystallization takes place, the degree of capture of the radioelement does not practically change in the case of adsorption, the degree of capture of the radioelement diminishes as well-formed crystals are obtained.

Numerous experiments were carried out to study the adsorption of polonium from solutions (20, 21,25). Minimum adsorption by negatively charged surfaces, such as glass, was recorded in a neutral and a weekly alkaline media; when polonium exists in a colloidal form. Polonium is adsorbed to a considerable extent in an acid medium as ions Po^{4+} or PoO^{2+}. Desorption by means of $1NHNO_3$ occurs the easiest when the absorption of polonium by glass has taken place from neutral or weakly alkaline solutions, as colloidal particles are combined with the sorbing surface less firmly than high-valent cations. Quartz glass and pyrex glass rich in silica possess the greatest capacity for sorption in relation to polonium. Preliminary treatment of glass with an alkali increases the adsorption of polonium, while acid treatment produces no tangible effect.

The adsorption of radium by glass was studied by many investigators (26). Reduced data on the solubility of radium sulphate were obtained because this phenomenon was not duly taken into account. Correct results were obtained by O.Erbakher and B.A.Nikitin (27). V.M.Vdovenko and A.G.Samoilovich (28) have shown that adsorption of radium on glass at concentrations of 10^{-7} - 10^{-11} mol/ml, with pH ranging from 2 to 7, is subordinated to Gui's theory, as applied to high-valent ions.

V.G.Khlopin (29) and his associates studied the adsorption of radium on a residue of lead sulphate. Particular attention was given to investigating the conditions for obtaining an adsorbent with a constant surface and - potential. The above-said researchers noted that adsorption of isomorphous ions was reduced to nothing but primary exchange adsorption, i.e. kinetic exchange with the ions of the surface. The presence of surface active substances in the solutions impedes the process.

A study was also made of adsorption of uranium by glass and paper filters, which is important in analytical work (30). Adsorption on glass proved insignificant and diminished in proportion to an increase in the concentration of acids or alkaline carbonate. Adsorption on filters grows as pH rises and reaches 7% in a "conditionally-neutral solution with a

concentration of uranium amounting to $5 \cdot 10^{-5}$ g/ml.

By comparing the adsorption and colloidal properties of a number of radioactive isotopes under investigation, it is possible to distinguish several typical cases (31):

1) The maximum of adsorption properties corresponds to a minium of colloidal properties, and vice versa (Po,Bi).

2) The maxima of adsorption and colloidal properties are coincidental (Ru, Tl^{3+}, Pm, La, etc.).

In the above two cases the elements form real colloids.

3) In the range of small pH, when there is no adsorption on glass or paper, a maximum of x colloidal properties (Zr,U) is recorded, Pseudocolloids are evidently formed in this case.

4) Adsorption of the radioelement grows in proportion to the increase in pH, and no maximum is formed on the adsorption curve (Tl^{1+}, Ra). There appears to be no colloidal phase in this case.

By comparing the adsorption and colloidal properties of radioelements, it has been possible to clarify their state in diluted solutions in many cases at different values of pH.

The adsorption and colloid-chemical properties of radioactive isotopes were studied by A.K.Lavrukhina (32) in connection with the processes of their coprecipitation with slightly soluble hydroxides ($Fe(OH)_3$, $Cd(OH)_2$, $Th(OH)_4$, etc.) and sulphides (FeS, Bi_2S_3, PbS, CuS, etc.). As is well known, these phenomena,

important for radiochemical analysis, are supposed to result eighter from mechanical capture by the precipitated residue of radiocolloids formed by radioisotopes, or from surface adsorption. It has been proved that coprecipitation of radioisotopes does not depend on the molar solubility of compounds used as carriers or the conditions of their precipitation. Of considerable importance is only the magnitude of molar solubility of the corresponding radioisotope compound. The degree of precipitation of the radiisotopes under investigation (Bi^{210}, Ce^{144}, Pb^{212}, Zr^{95}, Cu^{64}, etc) with the above hydroxides corresponds to the amount of precipitated hydroxide. The following mechanism of the process has been suggested: when pH is below the beginning of precipitation of hydroxides colloidal particles are formed of a non-isotopic carrier and of a radioisotope with similar adsorbed cations; the nuclei of the colloidal particles of the hydroxodes are merged during coagulation. The logarithm of the ratio between the molar solubility of the hydrooxide of some metal and the molar solubility of the radioisotope hydroxide points to the magnitude of coprecipitation of the radioisotope with the given hydroxide in the course of its precipitation.

Various phenomena related to new forms of radioactive transformations were the subject of intensive study in the USSR. B.V.Kurchatov, I.V.Kurchatov, L.V.Mysovsky and L.I.Rusinov (33) discovered in 1935 the phenomenon of nuclear

isomerism for artificially radioactive isotopes. These researchers obtained 36-hour bromine-82 by irradiating ethyl bromide with neutrons and ascertained that the formerly described 18-minute and 4.5-hour isotopes both correspond to brimine-80 whose nucleus, in addition to the basic state, may also be in a state of excitation.

Soon after O.Khan and F.Shtrassman (1939) discovered the fissionof uranium when the latter is acted upon by neutrons, the Soviet physicists K.A.Petrzhak and G.N.Flerov (34) proved that fission of the atomic nuclei of uranium may also take place spontaneously, at a speed, however, far below that of ordinary alpha-decay.

A cyclotron, the first in the Soviet Union and in Europe, was set up at the Radium Institute, by means of which a number of important investigations were carried out, and, notably, a study was made of the chemical nature of fission of heavy atomic nuclei. V.G.Khlopin, M.A.Masyik-Khlopina and N.F.Volkov (35) found in 1939 that on irradiating uranium compounds with neutrons, the fission products, collected by the method of recoil, evolve in the course of time radioactive gaseous products which proved to be krypton and xenon isotopes. It was proved, in contradistinction to the papers by other authors, that radioactive krypton and xenon are formed not only as primary products of the fission of uranium, but also appear in the subsequent stages of transformations of some fission pro-

ducts, such as radioactive isotopes of bromine, antimony, etc.

Numerous investigations were carried out in the USSR, devoted to the chemistry of individual natural radioactive and synthesized elements as well as radioisotopes.

B.A.Nikitin (36) developed the analytical chemistry of radium. A new method for radiochemical refining of protactinium has been suggested (37). Precipitation with the aid of amygdalic acid permits to isolate quite completely protactinium from a solution, purifying it at the same time of polonium, actinium, radium and thorium. The potentials of its deposition on platinum and gold were measured during investigations on the electrochemistry of polonium (38), and a study was made of the valent states in solutions, the phenomenon of disproportioning of quadrivalent polonium was found, and the electrode potentials of hexavalent polonium were determined. Using tellurium as a carrier, V.D.Nefedov and M.A.Toropova (39) synthesized dimethyldiiodopolonide, $(CH_3)_2Te(Po)I_2$, and proved by the method of isotopic exchange of iodine with CdI_x that in this compound the bond Te(Po) - I is of an ionogenic nature. Data have been obtained to the effect that $(CH_3)_2Po$ and $(CH_3)_2PoI_2$ are less stable than the corresponding tellurium compounds.

Considerable research was conducted on the chemistry of uranium and thorium compounds. A.A.Grinberg (40) and his

associates studied the properties of the oxalates of these elements. It has been shown that the oxalate of quadrivalent uranium, $U(C_2O_4)_2 \cdot 6H_2O$ represents an acid with pH of the saturated solution equalling 4.3. The oxalate of thorium, $Th(C_2O_4)_2 \cdot 6H_2O$, to all intents and purposes possesses no acid properties. Uranium oxalate is dissociated according to

$$/U(C_2O_4)_2(H_2O)n/ \quad /U(C_2O_4)_2(H_2O)n-1(OH)/^- + H^+,$$

and thorium oxalate according to

$$Th(C_2O_4)_2 \quad ThC_2O_4^{2+}.$$

Various salts of uranium-oxalic acid were synthesized and their coordination structure established.

Physico-chemical analysis ofuranyl oxalate has shown (41) that this compound, too, is dissociated according to

$$/UO_2C_2O_4(H_2O)/ \quad /UO_2C_2O_4(OH)/^- + H^+.$$

Uranyl oxalate may be considered as an acid equal in strength to carbonic acid.

Oxalate complexes of uranyl also possess acid properties in aqueous solutions, which diminish in the series

$$UO_2C_2O_4 \cdot 3H_2O \quad K_2/UO_2(C_2O_4)_2/ \cdot 3H_2O \quad K_6/(UO_2)_2(C_2O_4)_5/ \cdot 10H_2O$$

The constants were measured of the non-stability of the above complex anions.

The properties of some other oxalate derivatives of uranyl were described (42), such as ammonium dioxalatediaquouranyl $(NH_4)_2/UO_2(C_2O_4)_2(H_2O)_2/$.

I.I.Chernyaev (43) and his associates elaborated a method

for synthesizing aqueous uranyl monocarbonate, $UO_2CO_3 \cdot H_2O$, from aqueous solutions of uranyl nitrate under the pressure of CO_2. Anhydrous uranylcarbonate was obtained from suspensions of UO_3 when CO_2 is passed through under normal conditions.

O.E.Zvyagintsev and B.N.Sudarikov (44) established the composition of uranyl and thorium salicylates, $NH_4/UO_2(Sal^-)_3/ \cdot 4H_2O$ and $ThO(Sal^-)_2$, and defined some of their properties. Thorium salicylate is stable only in weakly acid medium (pH amounting to 4-5). Its solubility is rather slight. The compound rapidly hydrolyzes in a neutral or alkaline medium without a surplus of salicylate ions, forming thorium oxisalicylates. When there is a surplus of Sal^- ions, a soluble complex salicylate of the composition of $/ThO(Sal^{2-})_2/^{2-}$ is formed, which easily hydrolyzes while being heated. Uranyl salicylate is by far more soluble and stable, which underlies the suggested salicylate and oxisalicylate methods of separating uranium and thorium.

V.I.Spitsyn, E.A.Ippolitova and their associates (1957) comprehensively studied the properties of uranates of alkali elements. The thermal stability of such elements increases during the transition from Li_2UO_4 to Cs_2UO_4, the greatest amount of heat of formation being, however, found in the case of potassium and rubidium uranates. Thermographic and roent-

X-Ray genophasic analysis of the processes of interaction between the alkaline carbonates and uranium oxides has shown that diuranates are, as a rule, formed in the first stage of the reaction, at a temperature of about 500°C; subsequently, depending on the excess of one of the reagents, these turn into normal uranates or into more acid polyuranates. Basic uranates have been obtained of the composition of $Me^{I}_4UO_5$. A roentgeno-structural examination of normal uranates has shown that they contain tetragonal or pseudotetragonal layers of $(UO_2)O_2$ between which the atoms of the alkali elements are disposed. Endless chains of octahedrons of UO_6, linked by common ribs, were found in the structure - Na_2UO_4. When polyuranates were reduced by hydrogen, identified potassium and sodium uranates (V) of the composition $Me^{I}UO_3$ were also obtained, as well as uranate (IV) for rubidium, Rb_2UO_3. Analysis of the precipitated uranates of various alkaline elements has shown that analogous compounds are formed at approximating values of pH, irrespective of the nature of the hydroxide. As a result of washing off excessive of alkali with water, their composition regularly changes during the transition from lithium salt to cesium salt, tending to form more acid uranates. A similar regularity was disclosed in analysing the composition of normal uranate hydrolysis products.

Reactions of interaction between uranyl nitrate and

hydrogen peroxide were analysed in solutions (45). It has been shown that a peracid of the composition of $H_2U_2O_9$ is formed, which produces salts of the $NaHU_2O_9$ and $Na_2U_2O_9$ types. In other conditions a formerly known salt $Na_4UO_8 \cdot 9H_2O$ is obtained, for which solubility in water and in solutions of NaOH and HNO_3 was measured. The said salt enters into reactions of neutralization with HNO_3 and $NaHCO_3$:

$$Na_4UO_8 + 2HNO_3 \rightarrow Na_2UO_6 + 2NaNO_3 + H_2O_2$$

$$Na_4UO_8 + 2NaHCO_3 \rightarrow Na_2UO_6 + 2Na_2CO_3 + H_2O_2$$

Compounds $Na_2U_2O_9 \cdot 6H_2O$ and $Na_8U_4O_{22} \cdot 3H_2O$ are the products of decomposition of salt $Na_4UO_8 \cdot 9H_2O$ during heating.

Many investigators measured the solubility of slightly soluble compounds of uranium and thorium, namely oxalate (46), arsenates (47), uranyl, uranyl and thorium phosphates (48), and others.

A study was made of uranium and thorium halides of the lowest valence. Conditions were elaborated to obtain quinquevalent uranium by an electrochemical method (49). It has been proved that, with pH amounting to 3.0, it is in the form of an ion of UO_2^+. S.A.Sokolov (50) and his associates defined the pressure of saturated vapour of UCl_4 at various temperatures and the pressure of disproportioning of $UOCl_2$ and UCl_3. Oxichloride of trivalent uranium, UOCl, was obtained and some of its properties were described. The process was

studied (51) of reducing thorium halides by means of hydrogen. Some properties of $ThCl_3$ and $ThBr_3$ were defined.

Various ~~researchers~~ investigators obtained new complex derivaties of uranium with organic substances. A.A.Grinberg (52) and his associates studied compounds of uranyl with 1.3 diketones. Uranyl benzoyl-acetonate, $UO_2(C_6H_5 \cdot CO \cdot CH \cdot CO \cdot CH_3)_2 \cdot 4H_2O$ was synthesized, and the conditions for obtaining uranyl acetylacetonate, $UO_2(CH_3 \cdot CO \cdot CH \cdot CO \cdot CH_3) \cdot H_2O$, were specified. Experiments aimed at obtaining volatile uranium hexacarbonyl produced no positive results. Many intra-complex compounds of uranyl with Schiff bases were synthesized (53). Some of them may find application in analytical chemistry.

The development of the atomic industry and of the techniques of accelerating elementary particles in the USSR has made available transuranium and fission products, a field in which extensive research has been carried out.

A.D.Gelman (54) and her associates studied the composition of oxalate complexes of trivalent plutonium and determined the constants of their non-stability by the method of ion exchange. Chemical method has been suggested to obtain trivalent neptunium, using rongalite as a reducing agent.

V.V.Fomin (55) has shown that oxalates of tri-quadri- and hexavalent plutonium, when kept under various conditions (in the air or in a vacuum, at 25°C and -80°C, both in light and in darkness) decompose under the effect of alpha- radiation of pluto-

nium. In this case Pu^{6+} passes into Pu^{4+}, and Pu^{4+} into Pu^{3+} under the influence of the evolving carbon monoxide. The oxalates turn into carbonates and, partly, into oxides. The polarographic method was applied to study the complex oxalates of plutonium (56).

M.M.Popov and M.I.Ivanov (57) measured the heat of formation of plutonium dioxide is formed. V.I.Grebenschikova and V.N.Bobrova (58) studied the coprecipitation of trivalent americium, $Am_2(SO_4)_3$, with K_2SO_4 and found that anomalous mixed crystals are formed in this system. The crystals have no lower boundary of mixing, down to a concentration of the microcomponent of 10^{-10} mol/l. No inner adsorption compounds are disclosed in this case.

Soviet researchers described the sulphate method of isolating plutonium and neptunium (59), based on the properties of Np^{4+}, Pu^{3+} and Pu^{4+} to coprecipitate with binary plotassium sulphate and lanthanum, $K_3La(SO_4)_3$. It was shown in the case of plutonium that anomalous mixed crystals are then formed since Pu^{4+} enters the crystal lattice of binary potassium and lanthanum salt, despite the different valence of lanthanum.

To separate neptunium and plutonium in a preliminary way, a method was suggested (60) of fractioned sublimation of tetrachlorides formed in the course of chlorinating dioxides. Further separation was based on the difference between the oxidation-

reduction properties of neptunium and plutonium when acidified by potassium bromate.

A method was elaborated (61) for isolating americium from fission waste solutions containing a fraction of rare earth elements. Coprecipitation of americium with potassium uranyl-tricarbonate, $K_4[UO_2(CO_3)_3]$, is used for the purpose. Americium is first ~~acidified~~ oxidized to a ~~quinque~~ hexavalent state by hypochlorite, ammonium persulphate or ozone. The tricarbonates are repeatedly coprecipitated in an oxidizing medium.

Spectrophotometric analysis (62) of the behaviour of americium ions in solutions has helped in discovering self-reduction of Am^{5+} to Am^{3+} by the products of decomposition of water under the influence of radiation of americium. A study was made of the process of disproportioning Am^{5+}, which occurs according to

$$3AmO_2^{+} + 4H^{+} \rightarrow 2AmO_2^{2+} + Am^{3+} + 2H_2O.$$

The hexavalent americium so formed is reduced under the effect of its own radiation up to Am^{5+}.

Electrochemical methods were elaborated (63) to isolate fine oxide layers of plutonium and indicator amounts of curium and americium.

Soviet researchers (64) conducted experiments aimed at obtaining einstenium and fermium isotopes by bombardment of the uranium target with nitrogen and oxygen nuclei in a cyclotron with poles 150 cm in diameter. The maximum energy of accelerat-

ed six-charged oxygen ions amounted to 120 Mev, and of five-charged nitrogen ions to some 100 Mev. Separation of the transplutonium elements so obtained was made by the chromatographic method. Irradiation of uranium with nitrogen ions resulted in obtaining the einsteinium isotope with a mass number of 247, and irradiation with oxygen ions produced the fermium isotope, identified by the period of half-life and the energy of the alpha-particles. The chromatographic method was helpful in isolating californium, berkelium and curium isotopes to the amount of several hundred atoms.

Among the radioelements of fission products, cesium-137 attracted great attention of Soviet researchers. B.A.Zaitsev, A.I.Grivkova, E.I.Malinina and others (1957) developed a method for preparing its highly active sources. Cesium-137 is extracted out of the elements of fission products on a residue of nickel-potassium ferrocyanide. The product is treated with diluted HNO_3, as a result of which the bulk of radioactive and chemical substances passes into the solution while cesium remains in the residue which is oxidized in such a treatment and is transformed into nickel-potassium ferrocyanide. Subsequent alkaline treatment permits to remove again a part of the substances, while cesium still remains in the insoluble remnant. Acid-alkaline treatment is repeated several times. The final insoluble remnant is subjected to thermal decomposition, following which cesium is quite

completely leached out by water. Most foreign radioisotopes remain then on the waste residue. The solution of cesium compounds is neutralized by diluted HCl and evaporated. If required, additional purification of chemical substance is effected, based on the difference in the solubility of cesium chloride and chlorides of other alkaline elements. The above method has made it possible to obtain preparations of cesium-137 with a specific activity of 20 curie/g at a radiochemical purity of 99.9%.

Among synthesized elements, technetium presents now a considerable interest. The great progress achieved in the building of reactors permits to produce ever more powerful flows of neutrons. In this connection it may become practically profitable to obtain long-lived isotopes of technetium-99 out of irradiated molybdenum.

In the Soviet Union, Y.B.Gerlit (65) investigated some chemical properties of technetium, using the short-lived isomer, Tc^{99m}, isolated out of Mo^{99}. The researcher studied the conditions of extracting technetium by various alcohols, ketones and amines. Many valent transitions of technetium were established and data obtained on its existence in a bivalent form. Other investigators (66) successfully used methylethylketone to extract technetium in thepresence of a salting out agent, namely K_2CO_3.

V.I.Spitsyn and A.F.Kuzina (1957) developed a method for

obtaining ponderable amounts of technetium out of molybdenum irradiated with neutrons, making use of magnetium-ammonium phosphate as a carrier. The method permits at once to separat technetium in an ammoniacal medium from the basic mass of molybdenum present there. Further separation of technetium and of the phosphate ion is based on the fact that when in a reduced state, technetium is not absrobed by phosphate residues For this reason magnesium-ammonium phosphate is dissolved in hydrochloric acid and hydrogen sulphide is added to the solution, as a result of which molybdenum is separated additionally and technetium is reduced. Subsequent precipitation of magnesium phosphate under these conditions no longer results in a capture of technetium by the residue. The solution is then evaporated and the volatile chlorides are removed from the dry remnant by heating. The substances remaining in the preparation are separated by the chromatographic method in a hydrochloric or nitric acid medium. After treating the filtrate with ammonia and hydrogen peroxide, ammonium pertechnate is isolated. The above-mentioned researchers obtained new data on the conditions of volatility of technetium at various oxidation treatment of its concentrates. A study was made of the reactions of coprecipitation of technetium with various hydroxides, sulphides and other compounds.

Research related to the production of [illegible]

radioisotopes without carriers has acquired an ever increasing importance in modern radiochemistry. N.P.Rudenko (67) and other Soviet scientists used for this purpose the methods of coprecipitation chromatography extraction, formation of complexes, electrical precipitation, etc.

V.I.Kuznetsov (68) widely used organic coprecipitants capable of precipitating microamounts of elements out of extremely diluted solutions, which makes it possible to isolate, for instance 10^{-6} g of the element out of a volume of several litres. The burning of the residues so obtained permits to produce a coprecipitated element in the state "without carrier." The above-mentioned researcher made a detailed study of the mechanism of such processes. In some cases the coprecipitation of the radioactive isotope and the precipitant takes place as a result of some chemical analogy in their composition (for example, coprecipitation of non-ponderable amounts of thallium with diphenyliodonium); sometimes the intra-complex salt of cation in a microconcentration precipitates with an organic compound, dissolving in it (for instance, radioactive isotope oxinate with phenolphthalein, beta-naphtol and similar substances); finally, in other cases the radiocolloid coprecipitates with colloid-chemical compounds (for example, coprecipitation of niobium, tantalum or tungsten with basic dyestuffs and tannin). A number of methods have been

elaborated to carry out such operations of coprecipitation, and new organic precipitants were recommended.

A.N.Murin and his associates (69) developed methods for enriching radioactive isotopes obtained by irradiating element-organic compounds with thermal neutrons or gamma-quanta. The radioisotope atoms, whichwere driven out of the preparation and which passed into an "inorganic form", were separated by the methods of extraction or adsorption. When tetraphenyl-germanium was irradiated with neutrons, the yield of Ge^{75} amounted to some 90%. To obtain Bi^{210}, it proved convenient to irradiate triphenyldichlorobismuth, $(C_6H_5)_3Cl_2Bi$, with neutrons. The factor of concentration was in this case of the order of 100. Still greater enrichment (10^3-10^4) was achieved by irradiating the organic compounds of germanium, arsenic and antimony with gamma-quanta with an energy of 265 Mev (braking radiation of a synchrotron).

V.D.Nefedov and M.A.Torpoova (70) have shown that carbonyls of metals are suitable for obtaining enriched radioisotopes of chromium, molybdenum and tungsten. The factor of enrichment was as high as 10^4. Carbonyls $Mo(CO)_6$ and $W(CO)_6$ proved suitable for isolating radioactive isotopes To^{99m} and Re^{188} formed during the beta-decay of Mo^{99} and W^{188} respectively.

The electrochemical method of enrichment was applied by N.P.Rudenko and Z.V.Pastukhova (71) in producing radioactive

isotopes of indium. Metal tin irradiated with neutrons was transferred into an intracomplex salt with 8-oxyquinoline, and its saturated solution in chloroform was subjected to the action of an electric field with a gradient of 3000v/cm. The greater part of the In^{113m} so formed deposited on the anode. Electrolysis was carried out of a saturated chloroform solution of a pyridine-rhodanine complex of cadmium, $/Cd(C_5H_5N)_4/(SCN)_2$.

In recent years the methods of chromatography and extraction have found wide application in radiochemical research. This necessitated the elaboration of scientific principles of such methods, with due account for the peculiarities of the radiochemical systems, the microconcentrations of radioisotopes.

B.P.Nikolsky (72) evolved a theory of ion exchange which takes into account the basic factors influencing the exchange absorption of ions by ionites, namely the pH, the nature, valence and concentrationof the interchangeable ions, the nature of the ionite and the composition of the solution. According to the theory, the coefficient of distribution of the microcomponent ion ( ) between the ionite and the solution does not depend on the concentration of the microcomponent when the salt background is constant:

$$\frac{\quad}{C_1} = K^{z1}\left(\frac{\quad}{C_2}\right)^{z1/z2} f(8) = \quad = \text{Const},$$

where and. are the amounts of the absorbed ions of the micro- and macrocomponent, C_1 and C_2 are the concentrations of the respective ions z_1 and z_2 their valence, and f( ) is the multiplier containing the coefficients of ion activity in the sorbent and in the solution. The numerical value of changes when the nature of the macrocomponent ion and its concentration change, as well as during the introduction of new ions of great concentration in the solution and during changes in temperature and pressure.

V.I.Paramonova and her associates (73) conducted a number of experiments on the application of the method of ion exchange by means of absorption curves to the study of the state of radioelements in a solution, the regions of existence of the complex compounds so formed, and the determination of their constants of non-stability. This method helped in clarifying the behaviour of Nb^{95} and Zr^{95} in sulphuric acid, nitric acid and other solutions: the existence of ions of a new type of A_2^+ was established for ^{90} when it formed a complex with lactic acid, and of A^0_3 molecules when there was an excess of addenda, No ions of the composition of A^{2+} were discovered.

A.K.Lavrukhina and her associates (74) studied the regularities of ion exchange chromatographic separation of rare earth element isotopes. A 3.6% solution of ammonium lactate

was used as an eluant. With an ultra-low concentration of the elements, their elution is peculiar of narrow peaks. The addition of an isotopic carrier results in a shift of the peaks with a tendency of slower elution, and deteriorates their shape. There may also occur a superimposition of the peaks of adjacent elements. The theory of separation of rare earth elements by the chromatographic method was developed by N.N. Tunitsky and his associates (75).

S.Y.Yelovich and V.N. Prusakov (76) proved that when studying radiometrically the chromatography of radioisotopes Ce^{144} and Sr^{90} on resin KY-2, with ultra-low concentrations (down to 10^{-9}N) and even with small volume speeds at which the current of the liquid moves, account should be taken of the phenomenon of ion diffusion. The speed of the diffusion processes proves to be of importance for the process as a whole.

The mechanism of the radioelement extraction processes and the connection of the extraction properties with the structure of the solvent was studied by many researchers. V.M.Vdovenko and his associates analysed the distribution of uranyl nitrate between an aqueous solution and diethyl ether in the presence of various salting out agents (sodium, potassium, magnesium, aluminium nitrates, etc.). The distribution coefficient of uranyl nitrate grows in proportion to an increase in the concentration of the salting out agent. At

equivalent concentrations of the ions, the salting out effect of the additions under investigation grew in proportion to the increase in the charge and the decrease in the radius of the cation. It has been established that uranyl nitrate passes into diethyl ether with 4 molecules of water and is to be found there in a molecular state. Solid phases of various composition, ranging from $UO_2(NO_3)_2 \cdot 3H_2O(C_2H_5)_2O$ to $UO_2(NO_3)_2 \cdot 3(C_2H_5)O$, are isolated out of the ether solution, depending on the given conditions. Tensimetric examinations have permitted to compute the heat at which ether molecules combine with uranyl nitrate. The conditions of extracting uranyl nitrate out of dibutyl ether were also analysed.

S.M. Karpachova and her associates (78) compared the effect of various salting out agents during the extraction of uranyl nitrate with diethyl and dibutyl ethers as well as with N butyl acetate. The quantitative definition of the effectiveness of the salting out agents has allowed to introduce the term "equivalent of salting out" (amount of salt, equivalent to one mol of uranyl nitrate in an equilibrium aqueous solution). A.M.Rozen (79) studied the thermodynamics of extraction equilibriums of uranyl nitrate. The same researchers (80) produced quantitative data on the process of extraction of uranyl nitrate with tributyl phosphate together with various solvents.

Radiochemical investigations played an important part

in studying the processes of atomic nuclei fission under the actionof elementary particles with high energy. Special methods of radiochemical analysis were elaborated, aimed at separating and identifying the radioactive isotopes so formed.

A.P.Vinogradov and his associates (81) carried out a great ~~deal~~ amount of work devoted to studying the nature of the products of fission of copper, silver, bismuth and some other elements by fast particles, protons and deutrons with an energy of 100-700 Mev. The application of the precision method of radiochemical analysis helped to discover some scores of new radioactive isotopes and to calculate the yield of individual isotopes during various nuclear transformations (fission, splitting, knock-out of light nuclei, etc.) By way of illustration, the yields of 240 isotopes (aminly from Sr^{89} to Eu^{154}) were defined when uranium was irradiated with protons possessing an energy of 480 Mev. In the case of thorium, 244 isotopes were discovered (from Se^{83} to Eu^{152}), and 252 in the case of bismuth (from Ga^{72} to Ba^{129}). The ~~curves of~~ yields of various isobars distributed according to their consecutive numbers have a dome-like shape. Their width amounts to 2-3 units of the consecutive number. The fission of nuclei by particles of high energy is characterized by a constant distribution of the charge, irrespective of the mass number of the fission products and the consecutive number

of the fissionable nuclei. The above research helped to clarify the mechanism of fissionof uranium and thorium nuclei under the effect of high-energy particles. It appears to be mixed: the excited nucleus evaporates a certain number of neutrons, following which the process of fission sets in. The excited fission products so formed in their turn evaporate neutraons,

B.V.Kurchatov and others (82) made a similar study of tungsten fission products, with deutr ons possessing an energy of 280 Mev. In this case, 28 radioactive isotopes were found, chiefly in the region of z = 33-52.

G.M.Gorodinsky, A.N.Murin and others (83) applied the chromatographic method to study long-lived isotopes of rare earths, obtained by irradiating tantalum on a synchrocyclotron with protons possessing an energy of 680 Mev. A definition was made of the half-life periods, the type and energy of radiation of the isotopes so discovered, including the new isotopes of gadolinium.

* * *

This paper, brief as it necessarily is, could shed light only on the major trends along which radiochemistry developed in the Soviet Union.

Twenty years ago, radiochemical science in the USSR was represented but by a small staff of the Radium Institute.

Today radiochemical research is being conducted at many institutes of the USSR Academy of Sciences and at industrial research institutes, at the chairs of higher educational establishments and at factory laboratories. Numerous staffs of research radiochemists and engineers have been trained. The scope of scientific work on radiochemistry is enlarged year in, year out, and the range of subjects is being extended in this country. Soviet radiochemists are proud of the fact that they actively participate, jointly with scientists of other countries, in furthering the peaceful application of atomic energy for the good of mankind.

Bibliography

1. V.I.Vernadsky, Journal of the Russian Academy of Sciences, 5, 61 (1911).

2. V.G.Khlopin, Reports of the Russian Academy of Sciences (A), 101 (1924).

3. V.G.Khlopin, Proceedings of theRadium Institute, 4, 34 (1938)

4. V.G.Khlopin, B.A.Nikitin, Z.anorg, allg.Ch., 166, 311 (1927).

5. A.P.Ratner, Proceedings of the Radium Institute, 2, 67 (1933)

6. V.G.Khlopin, A.G.Samartseva, Reports of the USSR Academy of Sciences, IV, 433 (1934).

7. A.G.Samartseva, Reports of the USSR Academy of Sciences, 33, 506 (1941).

8. B.A.Nikitin, Z.anorg.allg.Ch., 227, 81 (1936); Journal of General Chemistry 9, 1167, 1176 (1939).

9. B.A.Nikitin, Reports of the USSR Academy of Sciences, 24, 564, 567 (1939). Sciences, 39(1940) Journal of the USSR Academy of Sciences, Section of Chemical

10. B.A.Nikitin, E.M.Ioffe, Reports of the USSR Academy of Sciences, 85, 809 (1952); Reports of the USSR Academy of Sciences,60, 595 (1948).

11. V.G.Khlopin, B.A.Nikitin, Z.phys.Ch.(A), 145, 137 (1929).

12. V.G.Khlopin, M.A.Tolstaya, Journal of Physical Chemistry, 14, 941 (1940).

13. B.A.Nikitin, E.M.Ioffe, Journal of theUSSR Academy of Sciences, Section of Chemical Sciences, 383 (1942); 15, 191 (1943).

14. V.G.Khlopin, M.S.Merkulova, Reports of the USSR Academy of Sciences, 65, 6 (1949); 71, 4 (1950).

15. M.S.Merkulova, Journal of Physical Chemistry 29, 10 (1955); Journal of Inorganic Chemistry 3, 25 (1958).

16. M.S.Merkulova, V.I.Chastukhina, L.N.Burtseva, Reports of the USSR Academy of Sciences, 102, 1167 (1955);

M.S.Merkulova, S.A.Potapova, ibid, 103, 643 (1955);
M.S.Merkulova, T.S.Shevelkina, ibid., 103, 457 (1955);
M.S.Merkulova, S.A.Potapova, T.S.Shevelkina,
V.I.Chastukhina, Journal of Physical Chemistry,
31, 1056 (1957).

17. V.G.Khlopin, V.R.Klokman, Reports of the USSR
Academy of Sciences, 65, 1, 33 (1949);
Journal of the USSR Academy of Sciences
(Section of Chemical Sciences), 254, (1949).

18. V.G.Khlopin, V.R.Klokman, A.N.Murin, V.D.Nefedov,
Journal of the USSR Academy of Sciences
(Section of Chemical Sciences) 127 (1950).

19. V.R.Klokman, Journal of Inorganic chemistry, 3, 33 (1958).

20. I.E.Starik, Proceedings of the Radium Institute,
1, 29 (1930);
2, 91 (1933).

21. I.E.Starik, N.G.Rozovskaya, Reports of the
USSR Academy of Sciences, 107, 850 (1956)
I.E.Starik, N.I.Alekseienko, N.G.Rozovskaya,
Journal of the USSR Academy of Sciences
(Section of Chemical Sciences), 755 (1956); I.E.Starik,
N.I.Alekseienko, Journal of inorganic chemicstry,
1, 1676 (1956).

22. A.P.Ratner, Z.N.Simonyak, Collected Works on
radiochemistry, published by Leningrad University
17, (1955); A.P.Ratner, N.G.Rozovskaya,
V.Gokhman, Proceedings of the Radium Institute
of the USSR Academy of Sciences, 5, 148, inst.2 (195).

23. I.E.Starik, A.V.Kositsyn, Journal of Inorganic
Chemistry, 2, 444, 1171 (1947); I.E.Starik
L.B.Kolyadin, ibid. 2, 1432 (1957).

24. I.E.Starik, A.P.Ratner, I.A.Skulsky, K.A.Gavrilov,
Journal of Inorganic Chemistry, 2, 1175 (1957).

25. I.E.Starik, N.G.Rozovskaya, Journal of inorganic
chemistry, 1, 598 (1956).

26. I.E.Starik, A.M.Gurevich, Proceedings of the Radium
Institute, 3, 241 (1937);
B.A.Nikitin, V.M.Vdovenko, ibid. 256.

27. O.Erbakher, B.A.Nikitin, Z.phys.Chem.(A), 158, 216 (1932).

28 V.M.Vdovenko, A.G.Samoilovich, Acta Physicochim. URSS, 4, 613 (1936).

29. V.G.Khlopin, V.I.Kuznetsova (Brebenschikova), Journal of Physical Chemistry 13, 1145 (1939); V.G.Khlopin M.S.Merkulova, Journal of the USSR Academy of Sciences (Section of Chemical Sciences), 5 (1949).

30. I.E.Starik, A.S.Starik, G.G.Karsradze, G.A.Murina, I.A.Efros, Collected works on radiochemistry, published by Leningrad University, 7 (1955).

31. I.E.Starik, Journal of Inorganic Chemistry, 3, 7 (1958).

32. A.K.Larrukhina, Journal of Analytical Chemistry 10, 205 I(1955); 12, 41 (1957).

33. B.V.Kurchatov, I.V.Kurchatov, L.V.Mysovsky, L.I.Rusinov, Cpmpt, rend., 200, 1201 (1935).

34. K.A.Petrzhak, G.N.Flerov, Reports of the USSR Academy of Sciences, 28, 500 (1940).

35. V.G.Khlopin, M.A.Pasvik-Khlopina, N.F.Volkov, Reports of the USSR Academy of Sciences, 24, 117, 665, 847, 851, (1939); N.F. Volkov, 24, 528 (1939).

36. B.A.Nikitin, Proceedings of the Radium Institute, 3, 228 (1937)

37. I.E.Starik, L.D.Sheidina, Journal of Inorganic Chemistry, 3, 139 (1958).

38. B.P.Nikolsky, D.M.Ziv, G.S.Sinitsyna, V.I.Shestakov, Collected Works "35 years of the Khlopin Radium Institute of the USSR Academy of Sciences," 39 (1957).

39. V.D.Nefedov, M.A.Toropova, Collected Works on Radiochemistry, published by Leningrad University, 139 (1955).

40. A.A.Grinberg, G.I.Petrzhak, Proceedings of the Radium Institute of the USSR Academy of Sciences, 7, 17,50 (1956);
A.A.Brinberg, G.I.Petrzhak, L.I.Evteiev, Journal of

Inorganic Chemistry, 3, 204 (1958).

41. A.A.Grinberg, B.V.Ptitsyn, E.N.Texter, Proceedings of the Radium Institute of the USSR Academy of Sciences, 7, 74 (1956).

42. I.I.Chernyaev, V.A.Golovnya, G.V.Ellert, Journal of Inorganic Chemistry, 1, 2726 (1956).

43. I.I.Chernyaev, V.A.Golovnya, R.N.Schelokov, Journal of Inorganic Chemistry, 2, 1763 (1957).

44. O.E.Zvyagintsev, B.N.Sudarikov, Journal of Inorganic Chemistry, 1, 69 (1956); 2, 128 (1957).

45. A.M.Gurevitch, L.D.Preobrazhenskaya, E.V.Komarov, Journal of Inorganic Chemistry, 2, 2307 (1957); L.P.Ratner, A.M.Gurevitch, L.P.Polotenskaya, ibid, 2316; L.P.Polotenskaya, ibid., 2323

46. K.A.Bolshakov, S.S.Korovin, V.E.Plyuschev, T.A.Yermakova, Journal of Inorganic Chemistry, 2, 222 (1957).

47. V.G.Chukhlantsev, A.K.Sharova, Journal of Inorganic Chemistry, 1, 36 (1956).

48. V.G.Chukhlantsev, S.I.Stepanov, Journal of Inorganic Chemistry, 1, 478 (1956).

49. A.P.Ratner, P.I.Chaikin, Collected Works on Radiochemistry published by Leningrad University, 75 (1955).

50. S.A.Schukarev, I.V.Vasilkova, A.I.Yefimov, V.P.Kudryashov, Journal of Inorganic Chemistry, 1, 2272 (1956); S.A.Schukarev, I.V.Vasilkova, A.I.Yefimov, ibid., 2652; S.A.Schukarev, A.I.Yefimov. ibid., 2, 2304 (1957).

51. S.A.Schukarev, G.I.Novikov, N.V.Andreieva, A.N.Ryabov, Collected Works on Radiochemistry, published by Leningrad University, 65, 1955; S.A.Schukarev, G.I.Novikov, A.V.Suvorov, Journal of Inorganic Chemistry, 1, 1948 (1956).

52. A.A.Grinberg, A.D.Troitskaya, Proceedings of the Radium Institute of the USSR Academy of Sciences, 7, 5 (1956);

[illegible].Lavrentiev,

53. I.A.Savich, A.K.Pikaiev, I....Lebedev, V.I.Spitsyn, Journal of Inorganic Chemistry, 1, 2736 (1956).

54. A.D.Gelman, M.P.Mefodieva, Reports of the USSR Academy of Sciences, 117, 225 (1957).

55. V.V.Fomin, R.E.Kartushova, G.I.Rudenko, Atomic Energy, No.3, 117 (1956).

56. V.V.Fomin, S.P.Vorobieva, M.A.Andreieva, Atomic Energy, No.1, 63 (1958).

57. M.M.Popov, M.I.Ivanov, . tomic Energy, No.4, 360 (1957).

58. V.I.Grebenschikova,V.N.Bobrova, Journal of Inorganic Chemistry, 3, 40 (1958).

59. B.V.Kurchatov, V.I.Grebenschikova, N.B.Chernyavskaya, G.N.Yakovlev, Research in the field of geology, chemistry and metallurgy (Reports of the Soviet Delegation to the Internal Conference on the peaceful use of atomic energy) USSR Academy of Sciences Publishing House, 219 (1955).

60. I.K.Shvetsov, A.I.Vorobyov, ibid., 225.

61. G.N.Yakovlev, D.S.Gorbenko-Germanov, ibid., 230.

62. G.N.Yakovlev, V.N.Kosyakov, ibid, 237.

63. V.B.Dedov, V.N.Kosyakov, ibid, 250.

64. L.I.Guseva, K.V.Filippova, Y.B.Gerlit, V.A.Drugin, B.F.Myasoiedov, N.I.Tarantin, Atomic Energy, No.2, 50 (1956).

65. Y.B.Gerlit. Research in the field of geology, chemistry, and metallurgy (Reports of the Soviet Delegation to the International Conference on the peaceful use of atomic energy). USSR Academy of Sciences Publishing House, 202 (1955).

66. M.S.Faddeieva, O.N.Pavlov, V.V.Bakunina, Journal of Inorganic Chemistry, 3, 165 (1958).

67. N.P.Rudenko, Collected Works "The use of tracer atoms in analytical chemistry," 1955, USSR Academy of Sciences (1955); Journal of Inorganic Chemistry, 1, 109 (1956); ibid., 3, 167 (1958).

68. V.I.Kuznetsov, Journal of Analytical Chemistry, 9, 199 (1954); Session of the USSR Academy of Sciences on the peaceful use of atomic energy. Meetings of the Section of Chemical Sciences, 301 (1955).

69. A.P.Murin, V.D.Nefedov, E.I.Yefimova, Collected Works on Radiochemistry, published by Leningrad University, 155, (1955); A.N.Murin, V.D.Nefedov, ibid., 159; A.N.Murin, V.D.Nefedov, V.P.Baranovsky, D.K.Popov, Reports of the USSR Academy of Sciences, III, 806 (1956).

70. V.D.Nefedov, M.A.Toropova, Journal of Inorganic Chemistry 3, 175 (1958).

71. N.P.Rudenko, Journal of Inorganic Chemistry, 1, 1680 (1956). N.P.Rudenko, Z.V.Pastukhova, ibid., 1, 2164 (1956).

72. B.P.Nikolsky, Journal of Inorganic Chemistry, 3, 59 (1958).

73. V.I.Paramonova, Journal of Inorganic Chemistry, 2, 523 (1957); ibid., 3, 212 (1958); V.I.Paramonova, V.B.Kolychev, ibid., 1, 1896 (1956); V.I.Paramonova, A.S.Voievodsky, ibid., 1 1905 (1956); V.I.Paramonov, A.N.Sergeiev, ibid., 3, 215 (1958); V.I.Paramonova, S.A.Bartenev, ibid., 3, 74 (1958).

74. A.K.Lavrukhina, F.I.Pavlotskaya, A.A.Pozdnyakov, I.M.Grechischeva, Journal of Inorganic Chemistry, 3, 82 (1958).

75. N.N.Tunitsky, V.V.Nekrasov, E.P.Chernyaieva, Journal of Inorganic Chemistry, 3, 66 (1958).

76. S.Y.Yelovich, V.N.Prusakov, Reports of the USSR Academy of Sciences, 112, 684 (1957).

77. V.M.Vdovenko, Journal of Inorganic Chemistry, 3, 145 (1958); Collected Works "35 years of the Khlopin Radium Institute of the USSR Academy of Sciences", 24 (1957); V.M.Vdovenko, T.V.Kovaleva, Collected Works on Radiochemistry, 44, published by Leningrad University (1955). V.M.Vdovenko, M.P.Kovalskaya, T.V.Kovaleva, Journal of Inorganic Chemistry, 2, 1677 (1957); V.M.Vdovenko, T.V.Kovaleva, ibid., 2, 1682 (1957); V.M.Vdovenko, A.A.Lipovsky, M.G.Kuzina, ibid., 2, 970, 975 (1957)

78. S.I.Karpacheva, L.P.Kharkhorina, G.D.Agashkina, Journal of Inorganic Chemistry, 2, 961 (1957).

79. A.M.Rozen, Atomic Energy, No.5, 445 (1957).

80. S.I.Karpacheva, L.P.Kharkhorina, A.M.Rozen. Journal of Inorganic Chemistry, 2, 1441 (1957).

81. A.P. Vinogradov, I.P.Alimarin, V.I. Baranov, A.K.Lavrukhina, G.V.Baranova, F.I.Pavlotskaya, A.A.Bragina, V.V.Yakovlev, Session of the USSR Academy of Sciences on the Peaceful Use of Atomic Energy, meetings of the Session of Chemical Sciences, 97 (1955); L.P.Vinogradov I.P.Alimarin, V.I.Baranov, A.K.Lavrukhina, G.V.Baranova, F.I.Pavlotskaya, ibid., 132.

82. B.V.Kurchatov, V.N.Mekhedov, M.Y.Kuznetsova, L.N.Kurchatova, ibid., 120.

83. G.M.Gorodinsky, A.N.Murin, V.N.Pokrovsky, B.K.Preobrazhensky, N.E.Titov, Reports of the USSR Academy of Sciences, 112, 403 (1957).

THE USE OF PHYSICAL METHODS IN THE PHYSICO-CHEMICAL STUDY OF METAL INORGANIC POLYCOMPOUNDS

By Victor Spitsyn,
Professor of Moscow University,
Corresponding Member of the USSR
Academy of Sciences

Derivatives of aquopoly and heteropoly acids are the most important representatives of the inorganic polycompounds class. It is already for over 130 years that heteropoly compounds have been the subject of numerous investigations. Hundreds of their specimens have been synthesized. Many heteropoly acids and their salts have found valuable practical application. Yet some important problems of the chemistry of heteropoly compounds have not been sufficiently clarified to this day. These include, for instance, such problems as basicity of heteropoly acids, the mechanism and individual stages of formation of heteropoly compounds, the role of water in this process, and the structure of heteropoly compounds as a whole and of the structural units of their inner sphere in particular. The solution of these problems is also complicated by the fact that the structure of crystalline lattices of heteropoly compounds may differ from the structure of their molecules in solutions.

The application of various physico-chemical methods plays an important role in studying heteropoly compounds. M.N.Sobolev (1) investigated the properties of phosphotungstic acid in solution, employing the method of dialysis, cryoscopy, ebullioscopy and conductometry. He was the first to establish that the above heteropoly acid is not a double compound or an

isomorphous mixture, as suggested by some researchers, but represents a complex substance subject to dissociation in diluted solutions.

In measuring the curves of neutralization of phosphomolybdic and phosphotungstic acids, A.Miłati (2) arrived at the conclusion that these compounds possessed high basicity exceeding that of phosphoric acid. Similar results were obtained by A.Rosenheim and his associates (3) with regard to some unsaturated heteropoly acids.

A valuable contribution to the development of the chemistry of heteropoly acids was made by the physico-chemical research conducted by G.Jander and his associates (4). They achieved their results by applying the methods of diffusion, light absorption, and potentiometric, conductometric and thermometric titration. While studying the conditions under which heteropoly compounds are formed, they compared the behaviour of solutions of normal molybdates and tungstates in an acid medium. According to Jander's studies, when solutions containing salts of acids which form a heteropoly compound are acidified, as, for example, tungstate and arsenate, there first appears the anion of an aquopoly compound namely hexatungstate,

$$6(WO_4 \cdot aq)^{2-} + 7H^{+} = (HW_6O_{21} \cdot aq)^{5-} + 3H_2O$$

and only then, already in a strongly acid medium, a heteropoly compound is obtained:

$$2(HW_6O_{21} \cdot aq)^{5-} + H_2AsO_4^{1-} + 4H^{+} = (H_3W_6O_{21})_2(H_2AsO_4) \cdot aq^{7-}$$

The transition of ion $(WH_6O_{21}\cdot aq)^{5-}$ to ion $(H_3W_6O_{21})^{3-}$ corresponds to the transformation of paratungstate into metatungstate.

P.Sochay (5) applied the polarographic method to study the process of hydrolysis of silico-, phospho- and boro-tungstates, occurring under the effect of caustic alkali and resulting in heteropoly compounds. He has proved that a number of mobile equilibriums becomes established in this case. The reverse reactions of formation of unsaturated compounds proceed in a similar way when solutions of unsaturated heteropoly acid salts are acidified.

The author and his associates used tracer atoms and the method of isotopic exchange in studying the properties, structure and reaction capacity of some aquopoly and heteropoly compounds. The isotope methods were combined with various physico-chemical ways of investigation (dialysis, polarography, the study of spectra of light absorption in the ultra-violet and infra-red regions, etc.) As a result, it became possible to obtain new data on the properties and structure of aquopoly and heteropoly compounds and to gain some new ideas regarding their structure. An opinion was voiced that the process of formation of aquopoly and heteropoly compounds greatly depends on the propensity for hydrogen bond of the anions of acids, participating in the said reaction of formation of the complex. It may be assumed that hydrogenions fix the anions participating in the building of the

complex ion. Apart from this, account should be taken of the possible role of hydroxonium ions in the inner structure of aquopoly and heteropoly anions.

Of considerable interest is the problem dealing with the mechanism of the initial stages of the reaction which leads to the formation of heteropoly compounds.

By using the electrochemical method to obtain heteropoly compounds, V.I.Spitsyn and K.G.Koneva (6) have shown that the mixture of Na_2HPO_4 and Na_2WO_4 passes through a series of stages of formation of non-saturated heteropoly compounds or of their double salts with Na_2WO_4 in the anode space of the electrolyser with pH of the solutions being gradually reduced, before phosphotungstate of the saturated series appears. Interaction between NA_2WO_4 and phosphate ions has already been recorded with pH amounting to 7.5 - 7. The composition of the crystalline products evolved from the solutions after electrolysis depends on the magnitudes of pH so obtained as follows:

pH of solutions	7.2	6.3	5.0	4.0	3.0	2.8	2.3
Ratio P:W in crystalline products	1:3	1:6	1:7	1:8	1:8.5	1:11	1:12

Taking these results into account, it might be conceivable that interaction between phosphate and tungstate ions beings already in the alkaline medium when the acid tungstates are not yet formed. To check the correctness of this assumption, V.I. Spitsyn, F.M.Spiridonov and I.D.Kolly (1956) studied the

process of interaction between sodium phosphate, Na_2HPO_4, and standard sodium tungstate, Na_2WO_4, by the method of self-diffusion, using tracer atoms of phosphorus and tungsten, P^{32} and W^{185}. The techniques of investigation resembled the one developed by J.Anderson and K.Saddington (7) for measuring the coefficients of diffusion of tungstate ions at various rates of pH, using a tracer atom W^{185}. In our experiments, the solutions of Na_2HPO_4/Na_2WO_4 or their mixtures, tagged with radioactive isotopes were poured into capillaries with a soldered bottom, which were inserted in a solution of exactly the same composition, but without radioactive isotopes (Fig.1). As a result of self-diffusion, the concentration of tracer atoms decreased in the capillary. The coefficient of diffusion of the anions under investigation was computed by means of Fick's law. Normal sodium tungstate, $Na_2WO_4 \cdot 2H_2O$, was selected as a compound with a known molecular weight. The ionic weights of phosphotungstates were compared with the ionic weight of normal tungstate, provisionally taken as a unit.

At a temperature of 20°C and with pH about 8, the coefficient of diffusion of phosphate ion exceeds almost three times that of diffusion of the normal tungstate ion:

Ion	pH	Coefficient of diffusion, D, cm^2/sec
HPO_4^{2-}	8.3	$23.0 \cdot 10^{-6}$
WO_4^{2-}	8.4	$8.7 \cdot 10^{-6}$

If such a quantity of phosphorus-tagged Na_2HPO_4 is added to a 0.1 molar solution of Na_2WO_4 that the ratio P:W amounts to 1:12 or 1:6, the coefficient of phosphate ion diffusion abruptly diminishes and approximates the magnitude typical for tungstate ion:

P:W ratio	pH	Coefficient of diffusion of ion HPO_4^{2-}, D, cm^2/sec
1:12	8.4	$11.0 \cdot 10^{-6}$
1:6	8.1	$6.2 \cdot 10^{-6}$

By tagging both salts, Na_2HPO_4 and Na_2WO_4, with radioactive isotopes, we found that phosphorus and tungsten possessed in such conditions practically the same coefficients of diffusion:

P:W ratio	pH	Coefficient of diffusion, D, cm2/sec	
		phosphorus	tungsten
1:6	7.8	$6.3.10^{-6}$	$5.8.10^{-6}$

A radiometric definition of P^{32} and W^{185} with both of them being present was made with the use of aluminium filters, as the maximum energy of beta-radiation of P^{32} (E = 1.701 Mev) greatly exceeds the energy of radiation of W^{185} (E = 0.428 Mev). The method is outlined in the paper referred to above (6).

The said results lead to the conclusion that the ions of HPO_4^{2-} and WO_4^{2-} (or $WO_4^{2-} \cdot 2H_2O$) interact already in the alkaline region, with pH amounting to 8-9, forming a complex ion

with the mass approximating that of a single tungstate ion. It should be noted that compounds of this type have been mentioned in publications (8), as, for example, $1WO_3 \cdot P_2O_5$, $2WO_3 \cdot P_2O_5$, and $Na_2O \cdot 2WO_3 \cdot P_2O_5$, although so far they have been obtained only out of molten media. In an aqueous medium, the reaction between the ions of HPO_4^{2-} and WO_4^{2-} appears to occur as a result of the appearance of a hydrogen bond according to $(PO_4 \ldots O_4W)^{4-}$ or $(HPO_4 \ldots HOH \ldots OWO_2O \ldots HOH)^{4-}$.

On the other hand, V.I.Spitsyn and K.G.Koneva, by using the method of tracer atoms, have proved that sodium metatungstate, peculiar, according to Jander, of the anion $(H_3W_6O_{21})^{3-}$, aq does not interact directly with phosphate ions. The reaction occurs only during subsequent acidification of the mixture. Hence, Jander's supposition regarding the initial formation of aquopoly compounds and their subsequent reaction with complex-forming acids does not conform to the recently obtained experimental data. The processes of formation of aquopoly and heteropoly compounds occur in the solution simultaneously and in parallel to the lowering of pH.

The initial stages of the reactions to obtain heteropoly anions are to some degree accounted for by the above results. There still remains, however, much to be clarified as to the mechanism of the reaction of formation of paratungstates. V.I.Spitsyn and E.A.Torchenkova (9) studied this process with the aid of tracer atoms, using the radioactive isotope of tungs-

ton - W^{185} (period of half-life: 73.2 days).

The solutions of $NaWO_4$ and of non-active sodium paratungstate, brought up to a certain value of pH by adding a small quantity of HNO_3, were poured together and were kept for a fixed time at a constant temperature. In terms of tungsten, the concentration of the solutions of normal tungstate amounted to 0.02-6 mg/ml, and of paratungstate to 4-20 mg/ml.

The transformation of normal tungstate into paratungstate was detected by isolating into the residue of slightly soluble mixed sodium-cesium paratungstate of paratungstate which, according to our investigations, using the conventional formulae, has the composition $Na_2Cs_3Hs/H_2(WO_4)6/, 4H_2O$ and captures, as a result of adsorption, not more than 0.5-0.8% of Na_2WO_4 out of the solution.

It appeared that the exchange of tungsten between acidified normal tungstate and paratungstate does not occur instantaneously. Thus, with pH amounting to 6.8, which corresponds to the region of existence of paratungstate, the compound is not formed at once (Table 1).

Table 1

Speed of transformation of Na_2WO_4 into paratungstate

Temperature: 25°C; pH: 6.8

Duration of reaction	Transition of tungsten-185 from Na_2WO_4 to paratungstate, per cent
5 min.	4.4; 2.6 (average 3.5)
1 hour	9.7; 10.8 (ditto 10.2)
24 hours	20.6; 15.4 (ditto 18.0)
268 hours	55.6; 74.4 (ditto 65.0)

As stated below, the isotopic exchange of tungsten between paratungstate and the product formed during the acidification of Na_2WO_4 proceeds by far faster than the time taken to obtain the product. Hence it may be assumed that 3-10% of the exchangeable product is formed from Na_2WO_4 in a short period of time (5 min. - 1 hr.) at a temperature of 25°C, and 65% in 268 hours. Such a behaviour leads to a critical appraisal of the views expounded by Jander (10) and Souchay (11) on the mechanism of formation of paratungstate in solution, according to which, at pH amounting to 6-8, the normal tungstate ion, fixing the ions of hydrogen, instantaneously changes into a hexatungstate anion $(HW_6O_{21}\cdot aq)^{5-}$ corresponding to paratungstate.

The transformation of Na_2WO_4 into a product exchangeable with paratungstate is accelerated at low values of pH and is retarded with transition to a neutral medium (Table 2). At the same time the conclusion should be drawn that the normal tungstate ion exchanges very slowly tungsten atoms with the para-

tungstate ion.

Table 2

Influence of pH on the speed of transformation of Na_2WO_4 into paratungstate

Temperature: 25°C; duration of reaction: 5 min.

pH	Transition of tungsten-185 from Na_2WO to paratungstate, %
6.8	3.0; 4.5 (average 3.7)
5.8	22.5; 18.1 (ditto 20.3)
5.1	28.4; 28.2 (ditto 28.3)
1.5	61.0; 49.4 (ditto 55.2)

As the temperature rises, the speed of transition of Na_2WO_4 in paratungstate increases (Table 3).

Table 3

Influence of temperature on the speed of transformation of Na_2WO_4 into paratungstate

pH : 6.8 - 7.0

Temperature,	Duration of reaction, hours	Transition of tungsten-185 from Na_2WO_4 to paratungstate, per cent
25	1	3.5
50	1	25.9
25	24	18.0
50	6	52.0

Hence, the conclusion may be drawn that the reaction of forming paratungstate when a solution of normal tungstate is acidified is a complex process which occurs slowly and which possibly consists of several stages.

An important feature of paratungstates is that some of their properties considerably change when the aqueous solutions of these compounds are kept for a long time or heated. The electric conductivity of heated and then cooled solutions of sodium paratungstate is much higher than the initial one (12). Fresh solutions of sodium paratungstate are precipitated in cold by some reagents (13, 14), but they do not exhibit such reactions after heating.

Proceeding from polarographic studies, Souchay (11) expressed the opinion that there exist two kinds of paratungstate, one of which (A) is formed during acidification of normal sodium tungstate, and the other (B) during the dissolution of crystalline salt. It was assumed that the said modifications differed by their hydrate composition.

V.I.Spitsyn and G.N.Pirogova (15) studied the properties of sodium paratungstate solutions, depending on the conditions under which they are obtained, the temperature of heating and the time of keeping. For this purpose the methods of dialysis, polarography, chromatography and light absorption were applied.

The colecular weights of the ions present in 0.01 molar tungstate solutions were defined by dialysis through a cello-

phane membrane at 25°C. The molecular weight of a hydrated ion of normal tungstate ($WO_4^{2-} \cdot 2H_2O$ = 284) was taken as a unit of comparison. The fresh solution of crystalline paratungstate, $Na_{10}W_{12}O_{41} \cdot 28H_2O$ possessed a molecular weight of about 3000, which well corresponds to ion $W_{12}O_{41}^{10-} \cdot 28H_2O$ (M=3366). After the solution has been boiled, the molecular weight of the anions diminishes to 1500-1600, i.e. it is practically halved (Table 4).

Table 4

Coefficients of dialysis and molecular weights of some tungstate ions in solution

Compound	Characteristics of solution	pH	Coefficient of dialysis	Molecular weight, M
$Na_2WO_4 \cdot 2H_2O$		8.0	0.236	284
$Na_{10}W_{12}O_{41} \cdot 28H_2O$	Fresh	6.1	0.072	3000
$Na_{10}W_{12}O_{41} \cdot 28H_2O$	Heated for 8 hrs at 100°C	6.2	0.095	1600
$Na_2W_4O_{13} \cdot 10H_2O$		3.6	0.033	14000

The phenomenon so recorded may be expressed by the equation

$$Na_{10}W_{12}O_{41} \cdot 28H_2O \quad 2Na5/H_3O \cdot W_6O_{21}/ \cdot 12,5H_2O.$$

Evaporation results in the formation of crystalline paratungstate which, when in solution, again exhibits a doubled molecular weight.

When solution Na_2WO_4 is acidified with nitric acid, the

composition of the anions so obtained depends on pH and the duration of the reaction (Table 5). It is only in the region of pH amounting to 7.0-6.6 that hexatungstate ions are formed at once. With pH amounting to 6.3-6.1, ions with a molecular weight of 5000-10000 are the first to appear. Ten days later, the weight drops to 1500. Ions of the $(H_3O.W_6O_{21})^{5-}$. nH_2WO_4aq type of high molecular weight appear to be formed in this case. In the course of time they become subject to disaggregation, splitting off the lighter hexatungstate ions. This phenomenon is manifested still more distinctly during further acidification. If pH of the solution is brought down to 5.8-5.6, the molecular weight of the anions so formed at first reaches the enormous magnitude of 55000-120000, and after being kept for 10 days diminishes but to 14000. Such a molecular weight was exhibited in our experiments by sodium metatungstate, $Na_2W_4O_{13} \cdot 10H_2O$, which corresponds to ions polymerized approximately 12 times by $H_3O(HWO_4)_3(H_2WO_4(H_2O)_6)^{2-}$ or $/W_4O_{13} \cdot 10H_2O/^{2-}$ ions.

Table 5

Changes in the coefficients of dialysis and molecular weights of anions during the keeping of acidified solutions of Na_2WO_4

pH	Time of keeping the solutions (days)	Coefficients of dialysis		Molecular weights	
		Directly after acidification	After keeping the solution	Directly after acidifying the solution	After keeping the solution
6.6	19	0.166	0.129	1500	1300
6.3	19	0.102	0.174	5000	1600
6.1	14	0.072	0.180	9900	1500
5.8	6	0.029	0.062	55000	14000
5.6	11	0.016	0.058	120000	14000

The transformations detected in the tungstate solutions were likewise confirmed (16) by the polarographic method with the aid of Geyerovsky's micropolarograph. The results of the polarographic examinations are given in Table 6 and in Figs. 2 and 3. It should be noted that it is not the initial tungstate ions that are present in a strongly acid medium in which tungstates are, as a rule, subjected to polarography, but colloidal tungstic acid or metatungstic acid. In this respect Na_2WO_4 and a fresh solution of paratungstate behave in a similar way (potentials of half-waves: 0.16 V.), thus forming one and the

same product in an acid medium. A tungstate solution which has been subjected to boiling produces already a different polarogram with two waves ($E^{I}_{1/2} = 0.26$ and $E^{II}_{1/2} = 0.44$ v), which resembles to a great extent the polarograms of sodium metatungstate and metatungstic acid. By its structure the hexatungstate ion seems to be kindred to metatungstate and is likely to be its structural unit. The above transformation of paratungstate is polarographically recorded beginning with a temperature of 35°C and terminates at 80°.

Table 6

Polarography of tungstate solutions

Compound	Concentration of solution mol/l	Characteristics of solution	Potentials of half-waves (in volts) against various backgrounds						
			12 N HCl		CH_3COOH-CH_3COONa pH 4.6-5,6			1 N K_2SO_4	
$Na_2WO_4.2H_2O$	10^{-3}		-0.46						
$Na_{10}W_{12}O_{41}.28H_2O$	10^{-4}	Fresh	-0.46		-0.46	-0.90	-0.44		
$Na_{10}W_{12}O_{41}.28H_2O$	10^{-4}	Heated for 8 hours to boiling point	-0.26	-0.44	-0.40	-0.90	-0.44	-0.84	-1.04
$Na_2W_4O_{13}.10H_2O$	10^{-4}		-0.26	-0.44	-0.40	-0.90	-0.44	-0.84	-1.04
$H_2W_4O_{13}.9H_2O$	10^{-4}		-0.26	-0.40	-	-	-0.45	-0.72	-0.93

The same variations in the behaviour of fresh or heated paratungstate solutions are observed with pH amounting to 5.0-5.6 (acetate buffer) and against the background of K_2SO_4 (Fig.3). It has long since been known that more acid (by the WO_3 content) tungsten compounds are reduced more readily to a quinvalent state. This may account for the lower potential of the beginning of reduction (-0.26 v.) of metatungstic acid (experiments 3 and 4, Table 6) as compared with ordinary tungstic acid (experiments 1 and 2, Table 6). The latter is, however, also revealed during polarography as a product of partial decomposition in solutions of metatungstic acid, producing a half-wave with a potential of - 0.44 or 0.40 v. The presence of several waves on polarograms recorded in the medium of an acetate buffer and against the background of K_2SO_4 appears to be related to the presence of several equilibrium forms of tungsten compounds which are reduced (W^{6A} W^{5A}) at various potentials of half-waves. In the case of a neutral or a weakly acid medium, it is unlikely that one and the same anion passes through successive stages of deeper reduction.

The kinetics of transformation of paratungstate ions into hexatungstate ions may also be traced by means of absorption spectra. The experiments were conducted in the ultra-violet region (220-290m). Fresh solutions of sodium paratungstate produce a curve which drops down abruptly as the length of the wave increases (Fig.4). During the keeping of the solutions,

the drop of the curve in the region of 245-260 m is retarded, and a platform appears there, followed by a maximum with the length of the wave amounting to 256-257 m . This maximum increases slowly in the course of time and reaches a constant magnitude a month after the solution has been prepared. Subsequent observations during the year proved that there were no changes in the optical properties of the solutions.

Similar phenomena, though at a more rapid rate, take place when paratungstate solutions are heated to the boiling point (Fig.5). In three hours there appears a maximum in the region of the length of waves amounting to 256-257 m . Its height attains a constant magnitude after the solution has been boiled for 10 to 16 hours. The coincidence of the values of maximum of light absorption for solutions which have been kept for a long time and for those which have been heated leads to the assumption that the same process occurs in both cases: transformation of paratungstate ions into hexatungstate ions which are in correspondence with the above maximum. It is worth noting that in this case, too, similarity is revealed between hexatungstate and metatungstate: their spectra of absorption are quite approximate (Fig.3).

Directly after their preparation acidified solutions of Na_2WO_4 produce absorption spectra as curves which abruptly drop as the length of the waves increases. In the course of time a platform is revealed on the curves, and then a maximum. This

process occurs, however, slower than in the case of sodium paratungstate solutions.

Finally, it should be noted that fresh or boiled solutions of paratungstate behave in a somewhat different way in relation to anionites (16). The sorption of hexatungstate ions occurs to a markedly lesser degree, particularly in the case of small concentrations (Fig. 6).

Of great interest is the similarity of the studied properties of hexatungstate and metatungstate. The transition of paratungstate to hexatungstate during the boiling of the solution possibly represents an important intermediate stage of formation of metatungstates. On the other hand, hexatungstates are likely to be the most immediate products of metatungstate hydrolysis.

The above-described experiments demonstrate that a diluted aquopoly compound may have a different structure of the ion as compared with the initial substance. Apart from this, in the first stages of formation of aquapoly compounds there come into being highly polymerized anions which but gradually become subject to disaggregation.

On the basis of the new experimental findings so obtained, it is possible to consider in greater detail the problem as to the phenomena occurring during the acidification of solutions containing components likely to form heteropoly compounds. We shall express our opinion on this subject, proceeding chief-

ly from the analysis of tungsten derivaties which we have studied in greater detail and, notably, of paratungstates, metatungstates and phosphotungstates.

It has often been stated in publications (4) that the formation of an acid tungstate, an aquopoly compound of the paratungstate type, is the primary stage of the reaction occurring during the acidification of solutions of normal tungstates. And yet it has been pointed out by many researchers that the so-called "white hydrate" of tungstic acid, approximating $H_2WO_4 \cdot H_2O$ by its composition, precipitates in the initial stage of acidification of normal tungstate solutions, followed by its dissolution and the formation of acid salts, namely aquopoly tungstates. V.I.Spitsyn and K.G.Koneva (17) observed isolation of the residue of white tungstic acid in the range of pH amounting to 8-6 when phosphotungstates were obtained electro-chemically. G.S.Savchenko (18) recorded the formation of tungstic acid in the same range of pH when studying oxalate complexes of tungsten. Finally, the above results of the experiments on the dialysis of acidified solutions of Na_2WO_4 have shown that anions of high molecular weight, which undoubtedly contain a great deal of tungstic acid, are the first products of the reaction in question.

It may be thus assumed that the formation of tungstic acid, $H_2WO_4 \cdot H_2O$, is apparently the first stage of the reaction which occurs when aqueous solutions of normal tungstates are

acidified. It may be presumed that in a certain range of pH (8-6) the simultaneous presence is possible of both the ions of WO_4^{2-} which did not participate in the reaction and of the tungstic acid which was being formed. There occur processes of formation of aquopoly anions and of more complex heteropoly anions with the participation of tungstic acid and WO_4^{2-} ions. At the same time one should take into account the rise of concentration of hydroxonium ions, H_3O^+, in the solution, as well as the possible appearance of hydroxonium forms of tungstic acid, $H(H_3O)WO_4$ and $(H_3O)_2WO_4$.

In accordance with the above considerations, V.I.Spitsyn (19) suggested the following scheme of formation of paratungstate anions from normal tungstate with ph amounting to 8-6:

$$H_3O^+ \; 3WO_4^{2-} \quad /OH_3 \; \ldots \; (WO_4)3/^{5-}$$

$$/H_3O(WO_4)3/^{5-} \; \& \; 3(H_3O)2WO_4 \quad /OH_3 \; \ldots \; (WO_4)3\ldots(HWO_4 \cdot H_3O)_3(H_2O)_3^{5-}$$

From the viewpoint of the nature and stability of chemical bond, all the hydroxonium ions should be considered in this case as equivalent (Fig.7).

The salts of the composition $5Na_2O.12WO_3.21H_2O$, i.e. paratungstates, correspond to anion $/OH_3(WO_4)_3(HWO_4)(H_3O)_3(H_2O)3/^{5-}$. Due to the hydrogen bond, additional molecules of water may join the hydrogen atoms of hydroxonium ions, where the coordination number of hydrogen has not been used to the full. For example, sodium paratungstate has a composition of $Na_{10}W_{12}O_{41} \cdot 28H_2O$.

With pH below 5 (optimum conditions: 4.5-3.5), aquopoly compounds of tungsten, defined by the ratio $Me_2O:WO_3$ equal to 1:2.4 (paratungstates), are transformed, as is well known, into more acid compounds with the ratio $Me_2O:WO_3$ equalling 1:4 (metatungstates). Sodium metatungstate, $Na_2W_4O_{13}.10H_2O$ or $Na_6W_{12}O_{39}.30H_2O$, is a most important representative of this class of substances.

The above reaction may be represented as a process of aggregation of two hexatungstate ions (paratungstate) due to hydrogen bonds:

$$2/H_3O(WO_4)(WHO_4)(H_3O)(H_2O)_3/^{5-} \rightarrow 4H_3O + 3H_2O$$
$$/(H_3O)_3(WO_4.H_3O)_9(H_2WO_4)_3(H_2O)_9/^{6-}$$

A possible structure of the metatungstate ion, in line with such an approach, is given in Fig.8.

A.A.Babushkin, G.V.Tukhnevich, Y.F.Beryozkina and V.I.Spitsyn (1957) studied the infra-red spectra of absorption of various sodium paratungstate hydrates. Sodium paratungstate containing a normal quantity of combined water exhibited in the region of high frequencies (3000-3800 cm^{-1}) a complex band of absorption consisting of four components (Fig.9). The band as a whole is related to the manifestation of a hydrogen bond between the molecules of water. Individual maxima of this band (3260, 3380, 3460 and 3540 cm^{-1}) indicate that there are several forms of bond of water between one another, as well as a bond with the tungsten atom. These

maxima correspond to the molecules of water which are at distances of 2.6; 2.7; 2.9 and 3.1 A. Analysis of the spectra of absorption of sodium paratungstate solutions in D_2O has led to the conclusion that the hydrate of $Na_{10}W_{12}O_{41}\cdot 25H_2O$ contains water in three different forms of coordination. The result is in general agreement with the above scheme of formation of the paratungstate ion.

In the transition to lower hydrates, the coordination of water in paratungstate assumes another form. Simultaneously with this, the structure of the compound undergoes an abrupt change. Analysis of sodium metatungstate by the same method pointed to the presence in it of two forms of coordination of water. One of them, as in paratungstates, is effected in the form of a hydroxyl combined with the tungsten atom (W-OH).

As to heteropoly compounds, their structures, from the viewpoint of hydrogen bonds and oxonium groups, may be represented in the case of phosphotungstates as follows (19).

When normal tungstate is acidified in the presence of phosphate ions up to pH 6-7, phosphotungstate of the unsaturated series if formed with the ratio P:W = 1:12. The reaction appears to proceed according to the following scheme:

$(PO_4H\cdot\cdot\cdot WO_4\cdot\cdot\cdot H_2O)^{4-} \rightleftarrows H^{\oplus}$ $(PO_4H\cdot\cdot\cdot WO_4\cdot\cdot\cdot H_3O)^{3-}$

Further

$$/PO_4H(WO_4)(H_3O/^{3-} \rightleftarrows 2(H_3O)_2WO_4$$

$$\left\{\begin{array}{l} \overset{W}{OH_2\cdot\cdot\cdot O_4H\cdot\cdot\cdot OH_2} \\ \overset{H}{\vdots} \\ PO_4H\cdot\cdot\cdot WO_4H\cdot\cdot OH_2 \\ \vdots \\ \underset{W}{OH_2\cdot\cdot\cdot O_4H\cdot\cdot\cdot OH_2} \end{array}\right\}^{3-}$$

The salts of the composition $2Me_2O\cdot P_2O_5\cdot 6WO_3\cdot 16H_2O$ correspond to anion $/PO_4H(WO_4)(HWO_4)_2(H_3O)_3(H_2O)_2/^{3-}$. This complex anion may additionally include in its composition molecules of water due to the hydrogen bond with hydroxonium or WO_4^{2-} ions. The salts of this series are generally represented by the formula $2Me_2O\cdot P_2O_5\cdot 6WO_3\cdot 16H_2O$.

When the acidity of the medium is raised, the "white hydrate" of tungstic acid, $H_2WO_4\cdot H_2O$, manifests, as is well known, a propensity for transitionto a yellow hydrate, H_2WO_4. A decrease in the amount of combined water per 1 atom of tungsten is also recorded in the complex anions of aquopoly and heteropoly compounds as pH decreases.

In the case of phosphotungstates, an increase in the relative content of tungsten in heteropoly anions results in a greater role of the H_2WO_4 groups and a smaller number of hydroxonium ions in the complex anions. The following structures may be assumed for phosphotungstate ions of a

different degree of saturation with tungsten.

With pH amounting to 6.5-6, salts are formed with a ratio P:W = 1:6, which have a composition of the type $3Me_2O.P_2O_5.12WO_3.16H_2O$. The possible structure of their anion $/PO_4(H_2WO_4)6(H_2O)_3/^{3-}$ is shown in Fig.10.

With acidity of the solutions about pH 3, luteophosphotungstates are formed of the composition $3Me_2O.P_2O_5.18WO_3.18H_2O$ with a ratio P:W = 1:9. The assumed structure of their anion, $/PO_4(H_2WO_4)_9/^{3-}$, is shown in Fig. 11. The question regarding the doubled structure of the luteophosphotungstate anion, raised on the basis of crystallo-chemical research should be considered as being open to discussion. Experiments on diffusion do not confirm the doubled molecular weight of compounds of this type.

Finally, with pH amounting to 2.3-1.5, phosphotungstates of the saturated series are formed with a ratio P:W = 1:12, of the composition $3Me_2O.P_2O_5.24WO_5.30H_2O$ (in the case of natrium salt). The suggested structure of anion, $/PO_4(H_2WO_4)12(H_2O)_3/^{-3}$, is given in Fig.12.

Proceeding from the above considerations, heteropoly acids of the saturated series may be conceived as products of addition of 12 molecules of a metal acid to an anion of a non-metal acid according to $Hm/RO_4(H_2XO_4)_4(H_2XO_4)_8(H_2O)n/$, where R is the non-metal element forming the complex, m is the basicity of the acid which corresponds to it, and X is Mo or W. Four molecules

of H_2XO_4 join directly tetrahedron Re_4. The other eight molecule (8) of H_2XO_4 are connected to one another. In this case the hydrogen bonds must be of primary importance.

The suggested schemes of the structure of aquopoly and heteropoly compounds reflect the important role of water in the process of formation of these substances. The behaviour of water in the said compounds of several types was studied by means of isotopic exchange with D_2O and heavy oxygen water.

V.I.Spitsyn and Y.F.Beryozkina (20) investigated the isotopic exchange of deuterium and hydrogen between water containing approximately 2.3 molar per cent of D_2O and various hydrates of sodium para- and metatungstate. The heavy water used for the purpose had a surplus density of 2400-2600 . A batch of an aquopoly compound was introduced into a wighed amount of heavy water of a known density. The mixture was kept for a fixed time at a constant temperature, following which the water was removed from the solution and subjected to standard purification. Due to the slight solubility of sodium paratungstate, there was always present a solid phase on the bottom of the reaction vessel. For this reason the solution was carefully decanted before being distilled. A quantitative appraisal of isotopic exchange was made by measuring the density of the heavy water before and after the experiment. The density of the water was determined within 3 by the flotation method with the help of a hollow quartz float. Table 7 presents data

on the isotopic exchange between the heavy water and sodium paratungstate.

Table 7

Isotopic exchange of hydrogen between heavy water and sodium paratungstate, $Na_1OW_{12}O_{41}.27.56H_2O$

Temperature: 20°C.

No. of experiment	Composition of exchange mixture, g. Sodium paratungstate	Heavy water	Duration of experiment, hours	Participation of H_2O molecules in the exchange	Average
1	2.93493	4.28970	2	11.7	
2	1.19260	7.16239	2	10.0	11.0± 0.5
3	2.00967	7.31270	2	11.4	
4.	4.90522	6.73990	12	28.9	28.2± 0.4
5	4.96346	7.28052	12	27.5	

As can be seen from the above results, the exchange of hydrogen proceeds at a high speed. Forty per cent of the water entering into the composition of the whole of the batch is exchanged in two hours, although by the magnitude of solubility of paratungstate, the liquid phase is supposed to contain but 20-25% of the salt used in the experiment. The mobility of hydrogen is so great that in 12 hours the exchange in the solid phase attains 100%.

At the temperature of 100°C, the rate of exchange grows considerably. In an hour's time as much as an average of 17.5

molecules of water is exchanged out of a 28-water hydrate.

Partly dehydrated sodium paratungstate exchanges with heavy water at a much lower rate. The product of the composition $Na_{10}W_{12}O_{41} \cdot 9.4H_2O$, prepared at a temperature of 100°C, does not exhibit any propensity for exchange at room temperature. Heating the solution to 100°C makes 2.6 molecules of the water exchangeable. Paratungstate hydrates containing water to the amount of 4.3 H_2O and $2H_2O$ do not exchange at all with heavy water.

Sodium metatungstate was used as ordinary 10-water hydrate with a composition, according to analysis, of $Na_2W_4O_{13} \cdot 9.65H_2O$. Its capacity for exchange with heavy water was less pronounced than in paratungstate (Table 8). At room temperature, 7-8 molecules of water possess great mobility and exchange almost instantaneously. However, the remaining 2-3 molecules exchange by far slower. It is only in 336 hours that the exchange involves 9.3 molecules of the initial hydrate. At 100°C, heating for an hour suffices for a complete exchange of the water.

Table 8

Isotopic exchange between heavy water and sodium metatungstate, $Na_2W_4O_{13} \cdot 9.65\ H_2O$

Temperature: 20°C.

No. of experiment	Composition of exchange mixture, g		Duration of experiment, hours	Participation of H_2O molecules in the exchange	Average
	Metatungstate	Heavy water			
1	0.86169	5.99456	1	7.1	9.2 ± 0.3
2	1.85081	5.15554	1	9.1	
3	1.69152	5.94939	168	6.5	7.1 ± 0.3
4	3.08151	5.35909	168	7.7	
5	4.94161	8.57961	336	9.35	9.3 ± 0.1
6	4.51843	8.29535	336	9.30	

In partly dehydrated sodium metatungstate, $Na_2W_4O_{13} \cdot 4.1H_2O$, one and a half molecules of water do not participate in the exchange. The mobility of hydrogen in the product of further dehydration of sodium metatungstate, of a $Na_2W_4O_{13} \cdot 2H_2O$ composition, is very low. It is only during boiling that a slight exchange is recorded. This suggests the existence of water bridges which connect the peripheral part of the complex anion with its structural units located deep in the molecule. The break-up of such a bridge during dehydration of the substance appears to hamper the progress of hydrogen exchange.

V.I.Spitsyn and Y.F.Beryozkina (21) studied isotopic exchange between heavy water containing deuterium and an aqueous sodium salt of phosphotungstic acid of the saturated series, $3Na_2O \cdot P_2O_5 \cdot 24WO_3 \cdot 33H_2O$. The method of performing the experiments was similar to the one described for sodium paratungstate. At a temperature of $20^{\circ}C$, 33.9 molecules of H_2O, i.e. all the combined water of the initial heteropoly compound proved to possess a capacity for exchange within the accuracy of measurements ($\pm$ 1.5 mols of H_2O). The results so obtained are not sufficient to confirm the assumption regarding the presence of strongly combined water in the complex, similar, for instance, to the one corresponding to the atoms of hydrogen of salt $Na_3H_4/P(W_2O_7)_6/ \cdot nH_2O$, according to Miolati-Rosenheim's formula, which are difficult to replace. At a temperature of $99^{\circ}C$, a considerable part of the combined water of sodium phosphotungstate (27.0$\pm$ 1.7 mols) are exchanged in an hour's time, yet it is smaller than at room temperature. The partial dehydration of salt which takes place at a higher temperature appears to impede the penetration of the exchangeable molecules of heavy water deep into the complex anion.

The behaviour of the combined water of aquopoly compounds was also investigated by means of exchange with heavy oxygen water. V.I.Spitsyn, R.I.Aistova and V.N.Vasiliev (22) used for this purpose water containing 1.2% atomic % of O^{18}. The

degree of exchange was controlled mass-spectrometrically. It appeared that at a temperature of 20°C sodium paratungstate exchanged with H_2O^{18} not only the oxygen of its combined water, but the whole of oxygen contained in the salt under investigation as well. At a temperature of 95°C, the two phases of the exchange took place in less than an hour. Apart from this, a considerable fractioning of heavy oxygen was recorded in them experiments, which accumulated in the paratungstate anion to a greater amount than anticipated by distribution. It is worth noting that normal sodium tungstate, $Na_2WO_4 \cdot 2H_2O$, did not exhibit such fractioning. The authors of the above-cited paper suggested that the great mass of complex anion of paratungstate was the cause of greater accumulation of H_2O^{18} molecules in this compound. There are some published data on the fractioning of oxygen isotopes, as for instance during hydration of some ions in an aqueous solution. A general rule was expounded (23), according to which heavier atoms tend to accumulate in heavier molecules during the exchange.

Similar phenomena of isotopic exchange of oxygen were revealed by V.I.Spitsyn, A.V. Lapitsky, R.I.Alstova, D.Nishanov and V.A.Poholkin (1957) in the case of polyniobates and -tantalates. Heavy oxygen water was subjected to exchange at a temperature of 95°C with the following compounds diluted in it: sodium pentatantalate - $6.88Na_2O \cdot 5Ta_2O_5 \cdot 29.1H_2O$, sodium hexatantalate - $9.92Na_2O \cdot 5Ta_2O_5 \cdot 26.1H_2O$, potassium hexaniobate -

- $9.92Na_2O.3Ta_2O_5.26.1H_2O$, potassium hexaniobate - $7.04K_2O.6Nb_2O_5.22.1H_2O$, and potassium metaniobate - $0.96K_2O.Nb2O5.4.36H_2O$. The method for carrying out the experiments and taking the measurements was similar to the one described above for sodium paratungstate.

In the case of the niobates under investigation, equilibrium was attained in 5 hours, corresponding to equidistribution of O^{18} between the heavy oxygen water and all the niobate anions combined by oxygen. In the case of tantalates, an additional phenomenon was disclosed, namely the fractioning of oxygen-18, tending to enrich the salts with the isotope of oxygen. It is possible that the greater mass of tantalate anions, as compared with niobates, exercises the same influence as has been noted in the case of paratungstates.

The results of the experiments devoted to a study of hydrogen and oxygen exchange lead to the conclusion that in the aquopoly and heteropoly compounds all the hydrogen and oxygen atoms are well capable of exchanging with D_2O and heavy oxygen water. This does not preclude that in the said complex anions the water may be located along several different forms of coordination, though with approximate energies of bond. A further, more detailed study of the kinetics of hydrogen exchange is bound to clarify this point. At any rate, the suggestions put forward by a number of investigators regarding the existence of particularly firmly combined atoms of hydrogen in the anions

of aquopoly and heteropoly compounds were not confirmed by the experiments we conducted on isotopic exchange.

A detailed study of the processes of dehydrating aquopoly and heteropoly compounds of tungsten, made by the author of this paper and his associates (24,25), has shown that a considerable part of the water combined in them is removed in a reversible way. This testifies to the fact that under certain conditions the hydrogen bond between the radicals of WO_4^{2-} may be replaced by a bond of tetrahedrons of WO_4^{2-} due to the common atoms of oxygen. The last 1.5-2 molecules of water are the most difficult to remove from aquopoly and heteropoly compounds. The water in the heteropoly compounds appears to originate from hydrogen atoms combined with the central radical of anon-metal acid (for instance, PO_4^{3-}, SiO_4^{4-}). In aquopoly compounds it corresponds to the radicals of the inner sphere hydroxonium.

At the same time it should be noted that the said 1.5-2 molecules of water also split off in parts. In some heteropoly compounds the last amount of water to be removed forms $0.5H_2O$, which corresponds to one hydrogen atom. It may be supposed that this is the last ion of hydrogen out of the central anion of the acid forming the complex.

An important conclusion suggests itself from the proposed analysis of the structure of heteropoly acid anions, namely that their basicity should equal that of the non-metal acid forming the complex. And yet there is quite an amount of published

data on the possibility of obtaining heteropoly salts of high substitution in accordance with formulae which follow from the conceptions of Miolati-Rosenheim. Some researchers (26) have notably, attempted to prove that during the gradual action of alkali, normal salts of heteropoly acids are transformed into salts of high substitution, as for example salt $Na_3H_4/P(W_2O_7)6/$ which is transformed into salt $Na_4H_3/P(W_2O_7)_6/$ and so on up to $Na_7/P(W_2O_7)6/$. There is no doubt that more light should be thrown on these points, with new methods of investigation employed for the purpose.

V.I.Spitsyn and E.A.Fabrikova (27) used tracer atoms for studying the interaction between double-replaced sodium of phosphotungstate of the saturated series, $2Na_2O.P_2O_5.24WO_3.nH_2O$ and successively added amounts of NaOH. A sample of the above salt was tagged by means of P^{32}. The decomposition of sodium phosphotungstate during the action of NaOH, attended with the splitting off of phosphate and standard tungstate, was established by means of two methods (Table9). When the first method was applied, the product of the reaction was precipitated through the effect of quinoline acetate. The free phosphate remained in the solution. The use of tagged phosphotungstate made it possible to observe the process of decomposition by the growth of activity in the filtrate or its decrease in the residue. The second method was based on the fact established by the investigators that there was no isotopic exchange of phosphorus between

phosphotungstate and sodium phosphate. Tagged phosphate, Na_2HPO_4, with a known specific activity was added to alkalized solutions of stable sodium phosphotungstate. Mixing of the tagged phosphate ions with the ions of phosphate formed during the decomposition of the heteropoly compound results in the following: the reverse process of forming heteropoly anions, caused by adding hydrochloric acid and heating, occurs already with the capture of tracer phosphorus. The degree of decomposition which had taken place was calculated by the decrease in the specific activity of the phosphate added after the separation of the salts in an acid solution by precipitating potassium phosphotungstate. The coinciding results of applying the two methods point to the fact that the decomposition of sodium phosphotungstate into phosphate and sodium tungstate begins with pH amounting to 6, after the addition of 5 mols of NaOH per 1 mol of double-substituted salt. Complete decomposition of the heteropoly anion sets in after adding some 25 mols of alkali per 1 mol of phosphotungstate.

Table 9

Decomposition of sodium phosphotungstate into phosphate and sodium tungstate in solutions containing various additions of caustic soda.

Mole of NaOH added per 1 mol of salt	Atom ratio of Na:P in the solution	pH of solution	Splitting off phosphorus as phosphate from phosphotungstate, per cent	
			Method 1	Method 2
1	2	3	4	5
0	2 : 1	2.4	0	0
1	3 : 1	2.9	0	0
2	4 : 1	3.6	0	0
4	6 : 1	5.0	0	0
5	7 : 1	6.2	6.0	0
7	9 : 1	7.2	24.0	20.0
10	12 : 1	7.5	39.1	35.0
20	22 : 1	8.2	68.2	70.5
25	27 : 1	9.0	95.1	98.6

In accordance with these data, the chemical analysis of the products formed during the effect of 1 mol of NaOH on 1 mol of triple-substituted sodium phosphotungstate, $3Na_2O.P_2O_5.24WO_3.nH_2O$, has proved that a double salt of the composition

$Na_3[PW_9O_{31}]$ · $3Na_2WO_4 \cdot 21H_2O$ is formed in this case. Hence, caustic soda added even in small quantities produces a partial decomposition of the heteropoly anion and brings about its transition to a compound of the unsaturated series, but does not produce salts of high substitution.

Subsequently V.I.Spitsyn, I.D.Kolly and I.S.Bashkirova (1957) investigated in a similar way the isotopic exchange of silicon between potassium silicotungstate, $2K_2O \cdot SiO_2 \cdot 12WO_3 \cdot nH_2O$ and the gel of silicic acid tagged by means of the short-lived isotope of silicon, Si^{39} ($T_{1/2}$ = 2.8 hours). Finely ground powder of rock crystal was irradiated with neutrons in an uranium reactor for a day. Following this, the preparation was fused with caustic soda. The silicate so obtained was decomposed by hydrochloric acid. The gel of the silicic acid was washed of the impurities by repeated decantations. The batches of tagged silicic acid were boiled for an hour with the initial solution of potassium silicotungstate as well as with solutions of the compound, which had been preliminarily treated with minimum small amounts of caustic soda and brought up to an equilibrium value of pH. The solutions were then centrifuged, the centrifugate was acidified and the slightly soluble cesium of silicotungstate was precipitated. In the case of partial decomposition of the heteropoly anion with an increase in the pH of the medium, radioactive silicon penetrated into it due to isotopic exchange and was fixed in the anion during the acidification of the

solution. The nature of interaction between the initial salt and the added caustic soda could thus be judged by the activity of the isolated residue of cesium silicotungstate. The results are given in Table 10.

Table 10

Isotopic exchange of silicon between the gel of silicic acid andthe solutions of potassium silicotungstate with various values of pH.

Mols of KOH added per 1 mol of silicotungstate	pH of the solution	Participating in the isotopic exchange of silicon out of the silicotungstate anion, per cent
-	4	0
2	5.5	3
6	7.2	8
12	8.1	20

The conclusion may be drawn that potassium silicotungstate of the saturated series does not exchange silicon atoms with the residue of the silicic acid. The exchange is, however, disclose when two mols of alkali are added per one mol of silicotungstate which testifies to the beginningof the splitting off of the silicotungstate anion. It is just in this range of pH (5-6) that E.A.Nikitina (26) presumed the formation of high substi-

tution salts to take place. It would be more justified in assuming that unsaturated heteropoly compounds of the silicodecitungstate type or their double salts with standard tungstate are formed in this case. A considerable decomposition of potassium silicotungstate is recorded with pH amounting to 6, when it appears to turn into silicoheptatungstate. It should be noted that the experiments with tracer atoms point to a considerably greater stability of silicotungstates as far as the effect of alkalis is concerned than of phosphotungstates.

The above results make highly questionable the possibility of obtaining salts of high substitution through the interaction between caustic alkalis and heteropoly salts of a normal composition. On the whole, however, the problem of salts of high substitution, referred to in various publications, requires more thorough systematic checking.

Valuable information on the properties of heteropoly compounds have been obtained as a result of studying the isotopic and ion exchange between various heteropoly anions. Still more important results were provided by observing the isotopic exchange of the addenda of the inner sphere between equopoly and heteropoly compounds.

V.I.Spitsyn and E.A.Torchenkova (9) studied the isotopic exchange of tungsten between silicotungstic acid tagged with W^{185}, and phosphotungstic acid. The experiments were conducted with various values of pH (1.8; 4.4; 5.67). After the experi-

ment, the phosphotungstic acid was precipitated as a potassium salt (potassium silicotungstate is soluble). No absorption was recorded of the radiocomponent on the potassium phosphotungstate residue. With pH amounting to 1.5-1.6 and a temperature of 25°C, the exchange proceeded to the degree of approximately 20%, irrespective of the time of interaction (ranging from 5 minutes to 240 hours) (Table 11). It might be supposed that only a part of the tungsten atoms of the heteropoly anions is capable of participating in the exchange. Boiling makes it possible to raise the degree of exchange to 30% in 3 hours and to 50% in 16 hours. In this case a partial decomposition of the compounds already appears to take place. With pH amounting to 4.4-4.7, the exchange proceeds at a faster pace: about 60% in 5 minutes, and 100% in an hour's time (Table 12). Evidently the products of partial decomposition of the heteropoly acids exchange tungsten atoms with less difficulty.

Table 11

Isotopic exchange of tungsten between silicotungstic and phosphotungstic acids in an acid medium

Duration of experiment	Temperature, °C	pH of solution	Degree of tungsten exchange, per cent	
5 min.	25°	1.8	20.4; 22.2	(average 21.3)
1 hour	25°	1.8	13.1; 20.4	(average 16.7)
240 hours	25°	1.5	21.9; 21.0	(average 21.4)
3 hours	boiling	1.8	29.6; 29.3	(average 29.4)
16 hours	boiling	1.6	50.3; 35.1	(average 42.7)

Table 12.

Isotopic exchange of tungsten between silicotungstate and phosphotungstate acids in a weakly acid medium

Duration of experiment	pH of solution	Degree of tungsten exchange, per cent
5 min.	4.4	82.9; 74.0 (average 78.4)
1 hour	4.4	119.0; 85.5 (average 102.2)
240 hours	4.7	94.3; 100.2 (average 97.2)

The deduction should be made from the above experiments that the isotopic exchange of addenda of the inner sphere between two heteropoly anions may take place. The exchange increases during the partial decomposition of heteropoly compounds.

The exchange of addenda between two heteropoly anions was investigated at greater detail by V.I.Spitsyn and Y.I.Bykovskaya (28) who used for this purpose silicomolybdic acid and sodium phosphotungstate tagged with tungsten. The exchange appears to result in the formation of mixed heteropoly compounds, such as phosphomolybdenotungstates. The experiments were carried out in an acid medium at various temperatures. Phosphotungstate was precipitated as a potassium salt (the similar salt of silicomolybdic acid dissolves easily). The results of the experiments are shown in Table 13.

Table 13

Exchange of addends of the inner sphere between sodium phosphotungstate, $Na_2H/PW_{12}O_{40}/\cdot 16H_2O$ and silicomolybdic acid, $H_4/SiMo_{12}O_{40}/\cdot 9H_2O$

Tungsten and molybdenum content in initial solutions: 0.02 g/ml; temperature: 20°C; pH:1.6

Time, hours	Degree of exchange, per cent: 1st series of experiments	2nd series of experiments	Average	Time, Hours	Degree of exchange, per cent 1st series of experiments	2nd series of experiments	Average
0.25	9.3	9.3	9.3	96	34.7	35.0	34.8
1	11.3	11.3	11.3	120	32.5	33.8	33.2
3	12.5	11.1	11.8	144	33.3	32.6	33.0
6	9.1	7.6	8.4	168	32.7	48.3	40.5
24	9.0	9.1	9.0	192	45.9	46.0	46.0
48	25.4	24.6	25.0	216	-	55.5	55.5
	20.9	22.4	21.6	240	54.1	50.9	52.5

With pH amounting to 1.6 and a temperature of 20°C, the exchange proceeds for the first 15-60 minutes to approximately 10%. The degree of exchange does not alter in the following 24 hours. Then there is an abrupt increase in the degree of exchange up to 20-25%. Similar leaps to as high a value of exchange as 33-35%, 40-46% and 53-55% take place in 96, 168 and

216 hours respectively. Therefore the curve representing the course of exchange (Fig. 13) is of a stage-like nature. This points to the non-equivalence of bond of individual tungstate ions inside the heteropoly anions and leads to the assumption that the inner sphere of heteropoly compounds has a multilayer structure. The abrupt increase in the degree of isotopic exchange at definite intervals of time seems to be related to the beginning of exchange in a new layer of addends. Heating makes for an increased degree of exchange.

The results of the experiments on isotopic exchange are also in accordance with the assumptions stated above regarding the structure of heteropoly anions. The molecules of a metal acid, added directly to the anion of a non-metal acid, must be combined more firmly than the others.

Interesting results have been obtained by studying the isotopic exchange between phosphotungstates of saturated and non-saturated series. The experiments were made with pH amounting to about 3, at room temperature. The course of exchange was controlled by precipitating phospho-12-tungstate as a potassium salt. The corresponding salt of luteophosphotungstic acid is soluble. The results of the experiments are given in Table 14. In 192 hours the exchange proceeds by as little as 21%, while between two saturated heteropoly compounds (sodium phosphotungstate - silicomolybdic acid) the degree of exchange is as high as 50% during the same period of time. The recorded stage-

like nature of the increase in the degree of exchange confirms once more the assumption regarding the non-equivalence of the inner sphere in the heteropoly anion.

Table 14

Isotopic exchange of tungsten between phospho-12-tungstate and tagged sodium phospho-9-tungstate

Tungsten constant in initial solutions: 0.02 g/ml; temperature: 20°C; pH: 2.9.

No. of experiment	Degree of exchange, per cent									
	Time, hours									
	0.25	1	4	24	48	72	96	144	168	192
1	10.4	10.2	12.4	18.3	17.7	12.9	20.2	22.2	26.9	21.1
2	11.2	10.2	11.8	19.4	17.5	16.8	16.4	21.5	20.0	21.1
Average	10.8	10.2	12.1	18.8	17.6	14.8	18.3	21.8	23.4	21.1

The experiments devoted to studying the possible exchange of the central atoms of heteropoly compounds yielded negative results. The following systems were investigated; sodium phosphotungstate - phosphoric acid, sodium luteophosphotungstate - phosphoric acid, and sodium phosphomolybdate - silicomolybdic acid. All the above-enumerated phosphorus containing compounds were tagged by means of P^{32}. As already stated above, potassium silicotungstate of the saturated series does not exchange sili-

con atoms with the gel of silicic acid. The absence of exchange of the central atoms confirms the prevailing view that they are firmly combined deep in the inner sphere of the heteropoly anions.

The method of isotopic exchange is of considerable importance in ascertaining the genetic bond between isopoly and aquopoly compounds on the one hand, and heteropoly compounds, on the other. Proceeding from measurements taken by means of the method of self-diffusion of the molecular weights of tungstate ions formed in the solution with various values of pH, J.Anderson and K.Saddington (7) have proved unambiguously that ions of the composition of $W_2O_7^{2-}$ or $W_3O_{10}^{2-}$ are formed in a water medium. There is therefore no reason to suppose that such groups exist in heteropoly anions. It is more likely that aquopoly anions containing constitutional water andformed in a water medium are present in them. It is, however, not clear in this case whether paratungstate ions, their kindred hexatungstate ions or, finally, metatungstate ions are the structural units of heteropoly anions.

V.I.Spitsyn and E.A.Torchenkova (9) studied the isotopic exchange of tungsten between an acidified solution of $Na_2^{*}WO_4$ and some heteropoly compounds; sodium silicotungstate, $Na_4/SiW_{12}O_{40}/\cdot 14H_2O$, and sodium phosphotungstate, $Na_2H/PW_{12}O_{40}/\cdot 14H_2O$, and sodium phosphotungstate, $Na_3H/PW_{12}O_{40}/\cdot 17H_2O$. After adequate keeping of the mixed solutions, phosphotungstate was

precipitated as a slightly soluble potassium salt, and silicotungstate as a cesium salt. The experiments have proved that $Na_2\overset{*}{W}O_4$ easily exchanges tungsten with the two heteropoly compounds under investigation in an acid medium. With pH amounting to 4.5 and a temperature of 25°C, sodium silicotungstate completely exchanges tungsten with an acidified solution of Na_2WO_4 in a few hours (5-24). For this reason similar experiments had to be conducted with pH of a higher value, so as to retard the formation of aquopoly compounds. With pH amounting to 6.1, the exchange of tungsten proceeds at a moderate rate (Table 15). The rise of pH to 6.8 retards the exchange to a still greater extent.

Table 15

Isotopic exchange of tungsten between an acidified solution of $Na_2\overset{*}{W}O_4$ and sodium silicotungstate

Temperature: 25°C; pH: 6.1.

Duration of experiment	Degree of tungsten exchange, per cent	
5 min.	1.7;	1.9 (Average 1.8)
1 hour	4.0;	3.8 (Ditto 3.9)
24 hours	15.4;	11.4 (Ditto 13.4)
77 hours	63.3	

Thus the conclusion should be drawn that the standard tung-

state ion does not exchange tungsten with heteropoly anions. The exchange proceeds with aquopoly compounds formed during the acidification of solutions of standard tungstate. This leads to the assumption that the WO_4^{2-} ion is not a structural unit of the heteropoly anions under investigation.

Experiments with sodium phosphotungstate and an acidified solution of Na_2WO_4 have shown that with pH amounting to 1.8 (2%), the isotopic exchange of tungsten proceeds at a faster speed and amounts to 85-90% in an hour's time. Paratungstate, tagged with tungsten^{185} and isolated from the solution as crystals, starts exchanging with phosphotungstate at a much slower pace than the acidified solution of Na_2WO_4. With pH at 2.25, the exchange amounts only to 25% in 24 hours.

It should be noted that the above-described isotopic exchange of tungsten between an acidified solution of Na_2WO_4 and heteropoly compounds takes place even in a strongly acid medium, i.e. when the heteropoly anion is still quite stable.

Highly interesting results were obtained from the experiments on the isotopic exchange of tungsten between phosphotungstic acid and tagged sodium metatungstate (9). With pH amounting to 1.3, when both compounds are quite stable, no exchange was recorded within error even on the expiration of 72 hours (Table 16). In a less acid medium (pH at 6.3), the exchange begins, however, to proceed, undoubtedly due to the partial decomposition of the

initial substances. The above experiments demonstrate that the nature of bond of the inner sphere addends in the metatungstate anion and phosphotungstic acid is quite different. Possibly there are differences also in the chemical structure of coordination anions.

Table 16

Isotopic exchange of tungsten between sodium metatungstate and phosphotungstic acid

Temperature: 25°C; pH:1.3

Duration of experiment	Degree of tungsten exchange, per cent		
5 min.	0;	9.8	(Average 4.9)
1 hour	4.6;	0	(Average 2.3)
774 hours	5.8;	1.0	(Average 3.4)
22 hours	0;	0	(Average 0)

By using the radioactive isotope of molybdenum, Mo^{99}, V.I.Spitsyn and Y.I.Bykovskaya (28) studied the rate of exchange of molybdenum between an acidified solution of $Na_2^{*}MoO_4$ and sodium phosphomolybdate. The course of the isotopic exchange was controlled by isolating into the residue slightly soluble potassium phosphomolybdate. The experiments have proved that sodium molybdate almost instantaneously exchanges molybdenum with phosphomolybdate in a strongly acid medium. With higher

values of pH, the rate of exchange is somewhat retarded. The conclusion may be drawn that that the bond of molybdenum in the phosphomolybdate anion is less firm as compared with the firmness of the tungsten bond in the phosphotungstate anion.

The above results of the experiments on isotopic exchange lead to the conclusion that the paratungstate ion and the metatungstate ion are hardly structural units of heteropoly anions. It is more likely that this role is directly played by tungstic or molybdic acid, as shown in the schemes suggested above. It follows from the paper by V.I. Spitsyn and G.N.Pirogova (15) that a great amount of tungstic acid joins the hexatungstate anion when Na_2WO_4 solutions are acidified.

Thus, proceeding from the results of the previous research carried out by other investigators, and using tracer atoms and new data from physical and chemical studies, it has been possible to advance the chemistry of heteropoly acids which are possibly the most intricate representatives of the class of complex compounds.

We do not deal in this paper with the problems of the structure of aquopoly and heteropoly compounds in a solid state, on which there is much valuable material obtained as a result of roentgenographic measurements. The task of our further research consists in establishing bonds between the structures of heteropoly compounds in solutions and in a crystal shape and bringing them to reciprocal conformity.

Conclusions

1. Tracer atoms were used to ascertain the primary stages of formation of aquopoly and heteropoly compounds, as well as for the purpose of studying their properties and structure by the methods of isotopic exchange. Along with this, other various physical and chemical methods of research were employed.

2. It has been established with the aid of tracer atoms that in acidified solutions of Na_2WO_4 the formation of paratungstate ions proceeds rather slowly and is accelerated with a slight rise of temperature (up to 50°C) and the lowering of pH.

3. The behaviour of sodium paratungstate solutions was studied under various conditions by means of several methods (dialysis, polarography, light absorption spectra, chromatography).

4. It has been shown that paratungstate ions, $W_{12}O_{41}^{10-} \cdot 28H_2O$, exist in fresh solutions, and that during the keeping or heating of the solutions they change to hexatungstate ions, $(H_3O \cdot W_6O_{21})^{5-} \cdot 12.5\ H_2O$, with half the molecular weight.

5. Hexatungstate ions or anions of high molecular weight, containing tungstic acid, are formed when Na_2WO_4 solutions are acidified, depending on pH, the anions being slowly subjected to the process of disaggregation.

6. It has been proved that the interaction between the HPO_4^{2-} and WO_4^{2-} ions begins already in the alkali region (pH

amounting to 6-9) and results in unsaturated phosphotungstates or their double compounds with normal tungstate.

7. Sufficient mobility of inner sphere addenda has been established in the anions of heteropoly compounds for isotopic and ion exchange to proceed between them.

8. A stage-like nature of isotopic or ion exchange in time has been recorded between two heteropoly anions, which testifies to the non-equivalence of the position of the inner sphere addenda atoms.

9. The isotopic exchange of the addenda in the inner sphere of some heteropoly anions with Na_2WO_4 and Na_2MoO_4 solutions has been investigated at various pH values, as well as with para-tungstate and metatungstate ions.

10. It has been established that the exchange proceeds with the least difficulty in the case of strongly acidified solutions of Na_2WO_4 and Na_2MoO_4. On the basis of these experiments it has been suggested that the addenda of the inner sphere in the heteropoly anions under investigation are the electroneutral molecules of tungstic or molybdic acids.

11. A study has been made of the interaction between sodium phosphotungstate and potassium silicotungstate, and caustic alkalis. It has been shown that with pH amounting to 5-6, hydrolysis of the complex anion commences. No formation of high substitution salts was revealed.

12. High mobility of hydrogen and oxygen atoms in a number

of equopoly and heteropoly compounds has been demonstrated by using the method of isotopic exchange and applying D_2O, which makes it rather an likely that "special" atoms of hydrogen or firmly combined water molecules exist in them.

13. By the infra-red spectroscopy method a great amount of hydrogen bonds has been disclosed in equopoly tungstates, as well as the presence of water in two or three forms of coordination.

14. It has been suggested that the process of formation of equopoly and heteropoly compounds is related to the appearance of hydrogen bonds between the anions of acids, which participate in the said interaction. The existence of oxonium groups in the structure of equopoly anions may also be assumed.

15. The structure of heteropoly compounds of the saturated series, of the phosphomolybdate or silicotungstate type, may be expressed by the general formula $H_m/RO_4(H_2XO_4)_4(H_2XO_4)_6(H_2O)_n/$ where R is the non-metal element in the formation of the complex, m is the basicity of the corresponding acid, and X is Mo or W.

THE USE OF TRACER ATOMS IN THE PHISICO-CHEMICAL STUDY OF SOME INOGENIC POLY-COMPOUNDS

By Victor Spitsyn

C A P S

Fig. 1. Diagram of device for studying the self-diffusion of phosphate and tungstate ions.

1) Glass capillaries, inner diameter 0.6 mm

2) Plexiglass holder

3) Plexiglass support

4) Stopper- holder

Fig. 2. Polarography against the background of 12 N HCl

1) $2.0 \cdot 10^{-3}$ mol/l $Na_2WO_4 \cdot 2H_2O$

2) $1.7 \cdot 10^{-4}$ mol/l $Na_{10}W_{12}O_{41} \cdot 28H_2O$

3) $1.67 \cdot 10^{-4}$ mol/l $Na_{10}W_{12}O_{41} \cdot 28H_2O$ (the solution was heated for 6 hours to boiling point)

4) $4.18 \cdot 10^{-4}$ mol/l $Na_2W_4O_{13} \cdot 10H_2O$. Sensitivity: 1/100

Fig.3. Polarography against the background of 1 N K_2SO_4

1) $4.62 \cdot 10^{-4}$ mol/l $Na_{10}W_{12}O_{41} \cdot 28H_2O$

2) $4.62 \cdot 10^{-4}$ mol/l $Na_{10}W_{12}O_{41} \cdot 28H_2O$ (the solution was heated for 6 hours to boilingpoint).

3) $3.08 \cdot 10^{-4}$ mol/l $Na_2W_4O_{13} \cdot 10H_2O$. Sensitivity: 1/10.

Fig. 4. Light absorption spectra.

1) $2.5 \cdot 10^{-2}$ mol/l $Na_2WO_4 \cdot 2H_2O$;

2) Fresh solution $2.5 \cdot 10^{-5}$ mol/l $Na_{10}W_{12}O_{41} \cdot 28H_2O$;

3) In 4 days; 4) In 11 days; 5) In 15 days; 6) In 18 days; 7) In 30 days; 8) In a year 9) $2.5 \cdot 10^{-5}$ mol/l $Na_2W_4O_{13} \cdot 10H_2O$.

Fig.5. Changes in the sodium paratungstate light absorption spectra, depending on the time of boiling the solution.

1) 1 hour; 2) 2 hours; 3) 3 hours; 4) 4 hours; 5) 6 hours; 6) 8 hours; 7) 16 hours.

Fig. 6. Absorption of paratungstate by anionite -10.

1) Fresh solution of $Na_{10}W_{12}O_{41} \cdot 28H_2O$;

2) Solution heated for 16 hours to boiling point.

Fig.7. Scheme of structure of hexatungstate anion.
Fig.8. Scheme of structure of metatungstate anion.
Fig.9. Spectra of infra-red absorption of various paratungstate hydrates.

1) $28H_2O$; 2) $19H_2O$; 3) $9H_2O$; 4) $4H_2O$; 5) $2H_2O$; 6) $0.2H_2O$ per mol of $Na_{10}W_{12}O_{41}$; 7) Dehydrated compound.

Fig.10. Scheme of structure of unsaturated phosphotungstate with ratio P:W = 1:6

Fig.11. Scheme of structure of luteophosphotungstate anion (ratio P:W = 1:9)

Fig.12. Scheme of structure of phosphotungstate anion of the saturated series (Ratio P:W = 1:12)

Fig.13. Exchange of addends between sodium phosphotungstate and silicomolybdic acid.

Bibliography

1. M.N.Sokolev. Journal of Russian Physical and Chemical Society 28, 186 (1896) (chemical section); Z.anorg.Chem. 12,16 (1896)
2. A.Miolati, Journ. prakt. Chem. 2, 77, 417 (1908)
3. A.Rosenheim, A.Traube, Z.anorg.Chem., 91, 57, (1915); A.Rosenheim, J.Jaenicke, Z.anorg.Chem., 101,249 (1917).
4. G.Jander, D.Mojert, Th.Adam, Z.anorg. allg. Ch., 180, 129 (1929) G.Jander, K.Jahr, W.Heukeshoven. Z. anorg. allg.Ch., 194, 383 (1930) G.Jander. H.Witzmann, Z.anorg.allg.Chem., 214, 145, 275 (1933) G.Jander, H.Spandau,Z.phys. Chem. (A), 187, 13 (1940); G.Jander, Z.phys. Chem. (A), 187, 149 (1940); G.Jander, F.Exner, Z.phys. Chem., (A), 190, 195 (1942).
5. P.Souchay, Ann. chim. (12), 2, 293 (1947); P.Souchay, J.Faucherre, Bull.Soc.Chim,Fr. (5), 18, 355 (1951).
6. V.I.Spitsyn, K.G.Kozeva. Journal of Inorganic Chemistry, 1, 2486 (1956).
7. J.Anderson, K.Saddington, J.Chem.Soc., 381 (1949).
8. J.Schulz, Z.anorg. allg. Chem., 284, 31 (1956)
9. V.I.Spitsyn, E.A.Torchenkova, Reports of the USSR Academy of Sciences, 95, 289 (1954).
10. G.Jander, U.Krnerke, Z.anorg.allg.Chem., 265, 244 (1951).

11. P.Souchay, Ann. chim., 18, 73 (1943); 19, 102 (1944); 20, 73 (1945).

12. Wells, J.Ann. Chem. Soc., 29, 112 (1907).

13. E.F.Smith, Chem. N., 137, 220 (1928).

14. V.I.Spitsyn, E.A.Torchenkova, Journal of Inorganic Chemistry, 1, 1794 (1956).

15. V.I.Spitsyn, G.N.Pirogova. Journal of Inorganic Chemistry, 2, 2102 (1957)

16. V.I.Spitsyn, G.N.Pirogova. Reports of the USSR Academy of Sciences, 115, 322 (1957)

17. V.I.Spitsyn, K.G.Komova. Journal of Inorganic Chemistry, 1, 941 (1956).

18. G.B.Savchenko. Selected articles on "Chemistry of Rare Elements," inst.2, p.63 (1955)

19. V.I.Spitsyn, Journal of Inorganic Chemistry 2, 502 (1957.

20. V.I.Spitsyn, Y.F.Beryozkina. Reports of the USSR Academy of Sciences, 108, 1068 (1956).

21. V.I.Spitsyn, Y.F.Beryozkina. Journal of Inorganic Chemistry, 1, 2642 (1956).

22. V.I.Spitsyn, R.I.Aistova, V.N.Vasiliev. Reports of the USSR Academy of Sciences, 104, 741 (1955).

23. M.Dole, Chem. Rev., 51, 263 (1952).

24. V.I.Spitsyn, I.D.Kelly, Reports of the USSR Academy of Sciences, 82, 239 (1952).

25. I.D.Kolly, G.N.Pirogova, V.I.Spitsyn, Journal of Inorganic Chemistry, 1, 460,470 (1956).

26. E.A.Nikitina. Journal of General Chemistry, 10, 779 (1940).

E.A.Nikitina, A.S.Kokurina. Journal of General Chemistry, 19,967 (1949)

27. V.I.Spitsyn, E.A.Fabrikova. Reports of the USSR Academy of Sciences 106,84 (1956).

28. V.I.Spitsyn, Y.I.Bykovskaya. Reports of the USSR Academy of Sciences 104, 256 (1956)

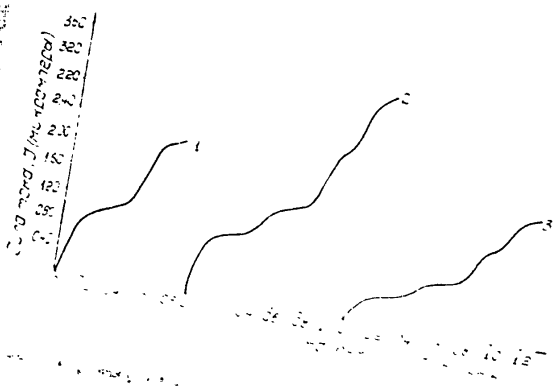


Fig. 3

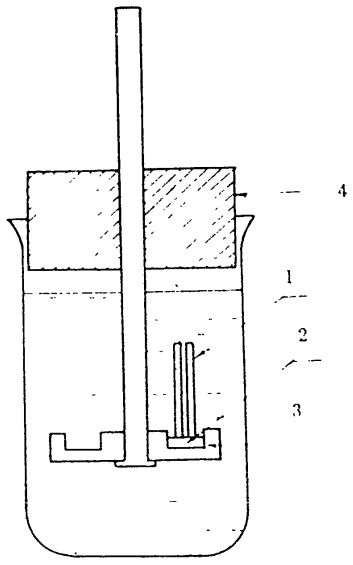


Fig. 1

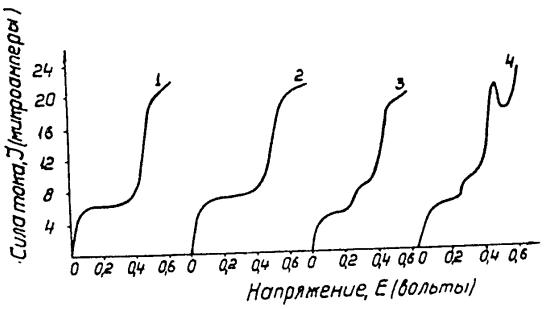
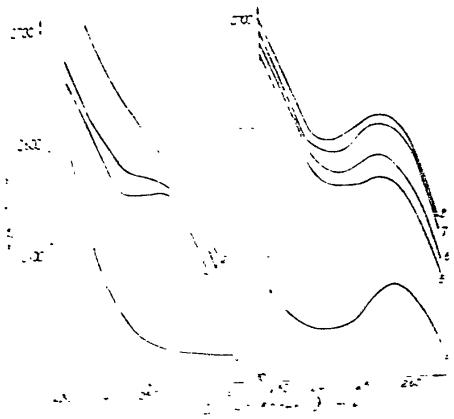


Fig 2.

Fig 5

Fig 4



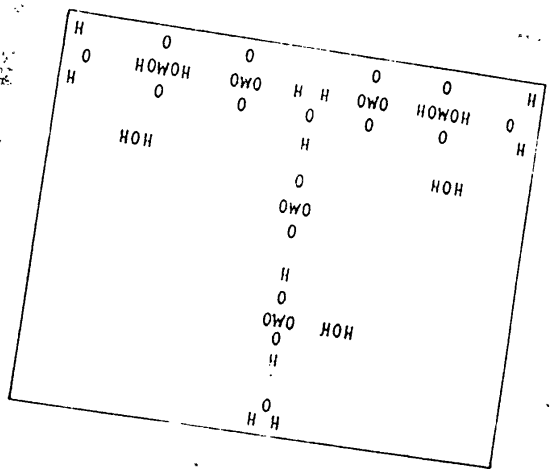


Fig. 7

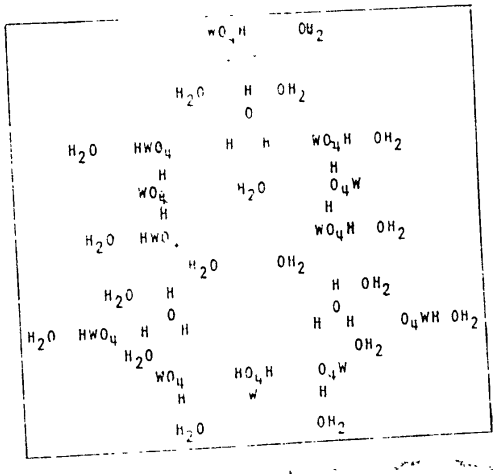


Fig 8

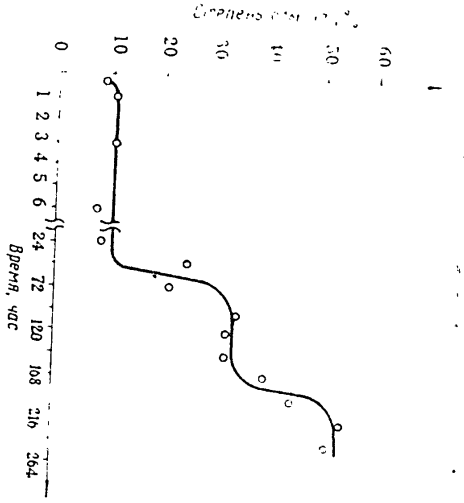


Fig. 13

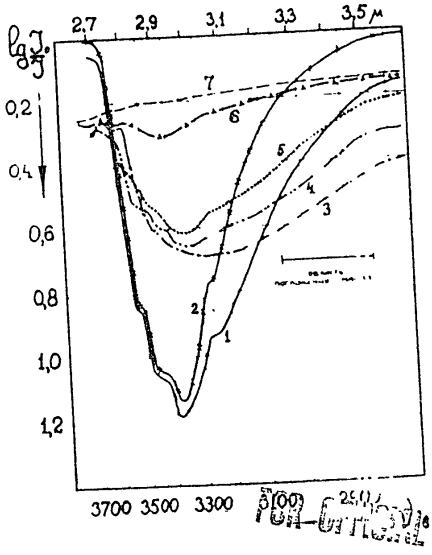


Fig. 9

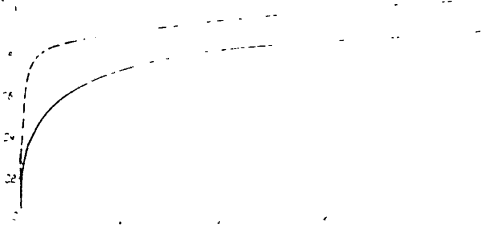


Fig 6.

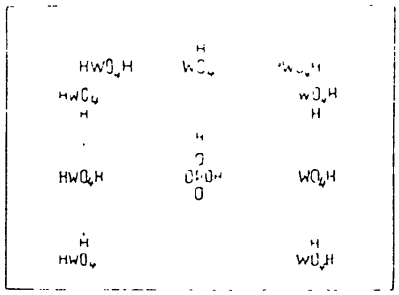


Fig 11

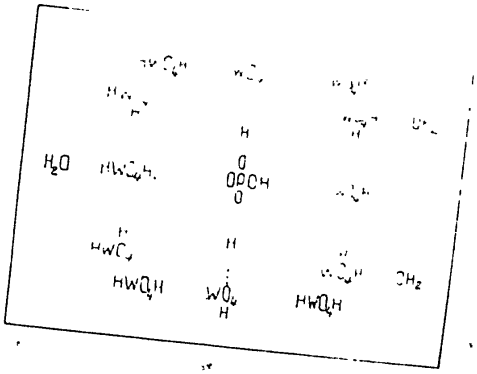


Fig 12

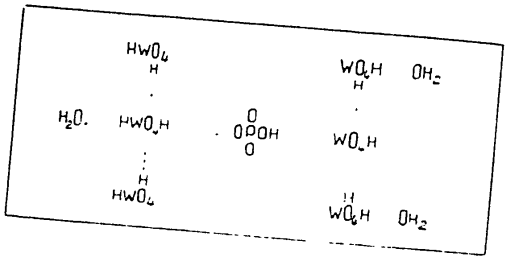


Fig. 10